Universidade de Aveiro
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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Doutor em Ciências e Engenharia do Ambiente, realizada sob a orientação científica da Doutora Célia dos Anjos Alves, Investigadora Auxiliar do Centro de Estudos do Ambiente e do Mar da Universidade de Aveiro e co-orientação do Doutor Casimiro Adrião Pio, Professor Catedrático do Departamento de Ambiente e Ordenamento da Universidade de Aveiro.

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palavras-chave

Queima doméstica, Queima de resíduos agrícolas e de jardim, Fogos florestais controlados, Partículas atmosféricas, Gases de combustão, Caracterização química, Traçadores orgânicos, Inquérito ao consumo de biomassa

resumo

Em Portugal, estima-se que 1.95 Mton/ano de lenha sejam utilizadas na queima doméstica para aquecimento e confecção de alimentos. Em simultâneo, nas últimas décadas, a área de floresta ardida também tem vindo a aumentar. Estes tipos de combustão contribuem para a libertação de quantidades elevadas de poluentes tóxicos que perturbam a química da atmosfera, interferem com o clima e possuem efeitos nefastos na saúde. A quantificação rigorosa, à escala regional e global, das emissões de gases e matéria particulada associada à queima doméstica, queima de resíduos agrícolas e fogos florestais é fundamental para vários fins, nomeadamente na investigação dos diversos processos atmosféricos, na elaboração de relatórios de emissões de gases de estufa, e na quantificação de fontes de poluição atmosférica que afectam a saúde humana. No sul da Europa, as bases de dados com factores de emissão detalhados são praticamente inexistentes. Os modelos climáticos, a modelização fotoquímica, os inventários de emissões e os estudos de identificação de fontes emissoras utilizam valores típicos obtidos para biomassa norte-americana ou do norte da Europa. Assim, é conveniente utilizar valores mais específicos obtidos localmente. Este estudo teve como principal objectivo a caracterização e quantificação dos gases e aerossóis emitidos por fontes de queima de biomassa, englobando as espécies lenhosas mais representativas da realidade nacional. Foram realizadas experiências de amostragem em laboratório (queima doméstica) e no campo (queima de resíduos agrícolas/jardim e fogos florestais controlados). Em laboratório, após selecção das espécies de biomassa e dos equipamentos de queima mais representativos em Portugal, estabeleceu-se um programa de amostragem para determinar os factores de emissão de poluentes gasosos e particulados, incluindo a composição orgânica e inorgânica dos aerossóis. Ao nível do campo, efectuou-se a amostragem das plumas de fumo resultantes da queima de resíduos agrícolas/jardim e de fogos controlados numa área dominada por espécies arbustivas. Os resultados deste estudo mostram que o tipo de equipamento de combustão e o tipo de biomassa utilizados têm um papel importante nos níveis e composição dos poluentes emitidos. Diferenças significativas entre o uso de equipamentos de combustão tradicionais versus equipamentos modernos foram observadas. Estas diferenças devem-se à maior eficiência de combustão dos equipamentos modernos, reflectindo-se na menor quantidade de matéria particulada, carbono orgânico e monóxido de carbono libertados. No que diz respeito ao fogo controlado em áreas dominadas por espécies arbustivas observou-se que a fracção orgânica estudada nas amostras de fumo é composta essencialmente por produtos resultantes da pirólise da vegetação.

Estes produtos são constituídos na sua maioria por esteredienos e derivados de esteróis, hidratos de carbono resultantes da quebra das moléculas de celulose, produtos alifáticos provenientes de ceras vegetais e metoxifenóis resultantes da degradação térmica da lenhina. A queima de resíduos agrícolas e de jardim, apesar de ser uma prática proibida no nosso país, é uma realidade bastante frequente. Para avaliar a composição das emissões de alguns tipos de resíduos foram recolhidas amostras de três tamanhos diferentes ($PM_{2.5}$, $PM_{2.5-10}$ and $PM_{>10}$). Apesar de se poder observar uma grande variabilidade em termos de compostos orgânicos dependendo do tipo de resíduo queimado, os compostos fenólicos (derivados do polifenol e guaiacil) e os ácidos orgânicos foram sempre predominantes em relação à restante fracção orgânica. O levoglucosano, o β-sitosterol e o fitol foram os traçadores de queima de biomassa detectados em quantidades mais apreciáveis na generalidade dos resíduos agrícolas e de jardim. O inositol pode ser considerado um bom traçador para as emissões resultantes da queima de rama de batata. Observou-se que as condições ambientais (tais como valores elevados de humidade relativa na atmosfera) provavelmente contribuíram para processos de coagulação e de crescimento higroscópico que influenciaram as características dos traçadores de biomassa, mudando sua distribuição para diâmetros maiores. Foi também feita a avaliação do consumo doméstico de biomassa na forma de um inquérito aplicado à escala nacional. Os resultados obtidos, conjugados com as bases de dados sobre factores de emissão obtidas nos ensaios de queima laboratoriais, permitiram estimar as quantidades emitidas de vários poluentes em cada distrito de Portugal continental.

Além de contribuir significativamente para o aperfeiçoamento dos inventários de emissões, os factores de emissão obtidos para vários compostos traçadores poderão ser aplicados em modelos no receptor de forma a avaliar a contribuição da queima de biomassa para os níveis de aerossóis atmosféricas e seus constituintes obtidos em campanhas de monitorização na Europa mediterrânea.

keywords

Residential wood burning, Agriculture and garden wastes burning, Experimental wildland fires, Atmospheric particles, Combustion gases, Chemical Characterisation, Organic tracers, Biomass consumption survey.

abstract

In Portugal, it was estimated that around 1.95 Mton/year of wood is used in residential wood burning for heating and cooking. Additionally, in the last decades, burnt forest area has also been increasing. These combustions result in high levels of toxic air pollutants and a large perturbation of atmospheric chemistry, interfere with climate and have adverse effects on health. Accurate quantification of the amounts of trace gases and particulate matter emitted from residential wood burning, agriculture and garden waste burning and forest fires on a regional and global basis is essential for various purposes, including: the investigation of several atmospheric processes, the reporting of greenhouse gas emissions, and quantification of the air pollution sources that affect human health at regional scales. In Southern Europe, data on detailed emission factors from biomass burning are rather inexistent. Emission inventories and source apportionment, photochemical and climate change models use default values obtained for US and Northern Europe biofuels. Thus, it is desirable to use more specific locally available data. The objective of this study is to characterise and quantify the contribution of biomass combustion sources to atmospheric trace gases and aerosol concentrations more representative of the national reality. Laboratory (residential wood combustion) and field (agriculture/garden waste burning and experimental wildland fires) sampling experiments were carried out. In the laboratory, after the selection of the most representative wood species and combustion equipment in Portugal, a sampling program to determine gaseous and particulate matter emission rates was set up, including organic and inorganic aerosol composition. In the field, the smoke plumes from agriculture/garden waste and experimental wildland fires were sampled. The results of this study show that the combustion equipment and biofuel type used have an important role in the emission levels and composition. Significant differences between the use of traditional combustion equipment versus modern equipments were also observed. These differences are due to higher combustion efficiency of modern equipment, reflecting the smallest amount of particulate matter, organic carbon and carbon monoxide released. With regard to experimental wildland fires in shrub dominated areas, it was observed that the largest organic fraction in the samples studied was mainly composed by vegetation pyrolysis products. The major organic components in the smoke samples were pyrolysates of vegetation cuticles, mainly comprising steradienes and sterol derivatives, carbohydrates from the breakdown of cellulose, aliphatic lipids from vegetation waxes and methoxyphenols from the lignin thermal degradation.

Despite being a banned practice in our country, agriculture/garden waste burning is actually quite common. To assess the particulate matter composition, the smoke from three different agriculture/garden residues have been sampled into 3 different size fractions ($PM_{2.5}$, $PM_{2.5-10}$ and $PM_{>10}$). Despite distribution patterns of organic compounds in particulate matter varied among residues, the amounts of phenolics (polyphenol and guaiacyl derivatives) and organic acids were always predominant over other organic compounds in the organosoluble fraction of smoke. Among biomarkers, levoglucosan, β-sitosterol and phytol were detected in appreciable amounts in the smoke of all agriculture/garden residues. In addition, inositol may be considered as an eventual tracer for the smoke from potato haulm burning. It was shown that the prevailing ambient conditions (such as high humidity in the atmosphere) likely contributed to atmospheric processes (e.g. coagulation and hygroscopic growth), which influenced the particle size characteristics of the smoke tracers, shifting their distribution to larger diameters. An assessment of household biomass consumption was also made through a national scale survey. The information obtained with the survey combined with the databases on emission factors from the laboratory and field tests allowed us to estimate the pollutant amounts emitted in each Portuguese district. In addition to a likely contribution to the improvement of emission inventories, emission factors obtained for tracer compounds in this study can be applied in receptor models to assess the contribution of biomass burning to the levels of atmospheric aerosols and their constituents obtained in monitoring campaigns in Mediterranean Europe.

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List of publications

This thesis is based on the work contained in the following papers:

I. Cátia Gonçalves, Célia Alves, Margarita Evtyugina, Fátima Mirante, Casimiro Pio, Alexandre Caseiro, Christoph Schmidl, Heidi Bauer and Fernando Carvalho, 2010. Characterisation of PM_{10} emissions from woodstove combustion of common woods grown in Portugal. Atmospheric Environment 44, 4474-4480.

II. Cátia Gonçalves, Célia Alves, Ana Patrícia Fernandes, Cristina Monteiro, Luís Tarelho, Margarita Evtyugina and Casimiro Pio, 2011. Organic compounds in $PM_{2.5}$ emitted from fireplace and woodstove combustion of typical Portuguese wood species. Atmospheric Environment 45, 4533-4545.

III. Célia Alves, Cátia Gonçalves, Ana Patrícia Fernandes, Luís Tarelho and Casimiro Pio, 2011. Fireplace and woodstove fine particle emissions from combustion of western Mediterranean wood types. Atmospheric Research 101, 692-700.

IV. Cátia Gonçalves, Margarita Evtyugina, Célia Alves, Cristina Monteiro, Casimiro Pio and Mário Tomé, 2011. Organic particulate emissions from field burning of garden and agriculture residues. Atmospheric Research 101, 666-680.

V. Célia Alves, Cátia Gonçalves, Margarita Evtyugina, Casimiro Pio, Fátima Mirante and Hans Puxbaum, 2010. Particulate organic compounds emitted from experimental wildland fires in a Mediterranean ecosystem. Atmospheric Environment 44, 2750-2759.

VI. Célia Alves, Cátia Gonçalves, Casimiro Pio, Fátima Mirante, Alexandre Caseiro, Luís Tarelho, Maria Carmo Freitas and Domingos Xavier Viegas, 2010. Smoke emissions from biomass burning in a Mediterranean shrubland. Atmospheric Environment 44, 3024-3033.

VII. Cátia Gonçalves, Célia Alves and Casimiro Pio, 2011. Inventory of fine particulate organic compound emissions from residential wood combustion in Portugal. Atmospheric Environment. Revised manuscript.

Abbreviations

BC	Black Carbon
BSTFA	*N,O*-bis(trimethylsilyl)-trifluoroacetamide
CCN	Cloud Condensation Nuclei
CO	Carbon Monoxide
CO_2	Carbon Dioxide
CPI	Carbon Preference Indices
DCM	Dichloromethane
EC	Elemental Carbon
EF	Emission Factor
EI	Electron Impact
GC-MS	Gas Chromatography Mass Spectrometry
HEPA	High Efficiency Particulate Air
HPLC	High Performance Liquid Chromatography
HULIS	Humic-like substances
ICP-MS	Inductive Coupled Plasma with Mass Spectrometry
ICP-OES	Inductive Coupled Plasma with optical emission spectrometry
MCE	Modified Combustion Efficiency
MFC	Mass Flow Controller
MP	Methoxyphenols
ND	Not Detected
NMHC	Non Methane Hydrocarbons
NO_x	Nitrogen Oxides
O_2	Oxygen
OC	Organic Carbon
OM	Organic Matter
PAH	Polycyclic Aromatic Hydrocarbons
PC	Pyrolysed Carbon
PHC	Phenolic Compounds
PM	Particulate Matter
PM_1	Particulate Matter <1µm

PM_{10}	Particulate Matter <10µm
$PM_{2.5}$	Particulate Matter <2.5µm
POM	Particulate Organic Matter
RWC	Residential Wood Combustion
SO_2	Sulphur Dioxide
SPE	Solid phase extraction
T	Temperature
TC	Total Carbon
TMCS	Trimethylchlorosilane
TOC	Total Organic Carbon
TOE	Total Organic Extract
UCM	Unresolved Complex Mixture
UV	Ultra Violet
VOC	Volatile Organic Compounds
XRF	X-ray Fluorescence Spectroscopy

CHAPTER 1

Chapter 1. General Introduction

Planet resources are used by all societies in order to improve their standard of living, a process commonly known as development. However, maintaining the success of this process compels society to ensure that the planet will continue to provide these resources, a practice better known as conservation. The search for a balance between these two concepts is in fact one of the greatest challenges facing Humanity at the present. If the planet is to be more productive and remain agreeable in terms of living conditions and housing, a detailed knowledge is necessary, about the natural and anthropogenic mechanisms and feedbacks with regard to human activities, as well as the processes in which food, water, air quality and many other resources essential to survival, are a direct result.

The anthropogenic activities are so extensively developed that the composition of reservoirs such as the atmosphere has undergone through irreversible changes. In fact, one of the consequences of these changes is the presence of very high concentrations of several pollutants in the atmosphere.

Directing attention to this problem, new goals with respect to renewable energy sources were set by different pieces of legislation. Until 2020, Europe will attempt to employ renewable energy sources in 20% of the total consumption of energy (EREC). The use of biomass for energy production is being promoted to decrease dependence on fossil fuels. However, biomass burning is one of the major sources of atmospheric particulate matter (PM). Additionally, in the last decades, in Portugal, the burnt forest area has also being increasing. It is well known that forest fires are one of the major sources of air pollutants (Ikegami et al., 2001; Lee et al., 2005; Pio et al., 2008; von Hoyningen-Huene et al., 1998). These combustions result in high levels of toxic air pollutants and a large perturbation on atmospheric chemistry, which has significant impacts on human health (Bowman and Johnston, 2005; Lighty et al., 2000; Naeher et al., 2007; Vedal and Dutton, 2006), regional to global air quality (Caseiro et al., 2009; Duck et al., 2007; Favez et al., 2009; Jaffe et al., 2008; Jeong et al., 2008; Legrand and Puxbaum, 2007; Liu et al., 2009; Wang et al., 2007) and climate (Chen et al., 2010; Hobbs et al., 1997; Langmann et al., 2009; Penner et al., 1990; Randerson et al., 2006).

1.1 The atmospheric aerosol

An aerosol is generally defined as a suspension of liquid or solid particles in a gas, with particle diameters in the range of 0.001 – 100 μm (Seinfeld and Pandis, 1998). In atmospheric sciences, the term aerosol traditionally refers to suspended particles that contain a large proportion of condensed matter other than water, whereas clouds are considered as separate phenomena (Pruppacher and Klett, 1997).

Atmospheric aerosol particles result from a mixing of natural and anthropogenic sources. Primary particles are directly emitted into the atmosphere from sources such as mineral dust, biomass burning, biological materials, incomplete combustion of fossil fuels and sea salt, among other sources. These particles retain much of the chemical properties of their sources. Secondary particles, on the other hand, are formed by gas-to-particle conversion in the atmosphere, through chemical reactions (nucleation and further coagulation and condensation processes). These particles may undergo great chemical changes. In this study, emphasis will be placed on primary particles, focusing mainly on the identification and quantification of compounds directly emitted from biomass burning.

1.1.1 Biomass burning: Background

Biomass burning emissions have a great expression on the planet. Since pre-historic times (Carboniferous) records of charcoal horizons in sedimentary rocks from forest fires are observed (Simoneit, 2002). Scientific interest in this topic grew when biomass burning began to rival fossil fuel use as a source of atmospheric pollution (Crutzen and Andreae, 1990; Seiler and Crutzen, 1980) and when it became evident that these emissions could affect large areas of the world as a consequence of long-range transport (Kirchhoff and Nobre, 1986; Reichle et al., 1986). Today, biomass burning has become a global problem, due to its broad range of uses: clearing of forests and brushlands for agricultural use, control of pests and weeds, production of charcoal, waste disposal, control of agriculture and garden wastes, energy production, cooking and heating, among others (Bond et al., 2004; Gelencsér, 2004; Simoneit, 2002).

Emissions from the combustion of any type of fuel depend directly on its chemical composition and the combustion conditions.

1.1.1.1 Biomass

The most used fuel in combustion processes is the wood. Burned wood comes from different tree species, but is essentially formed by three main components, apart from water (up to 60%). Cellulose is usually the major compound containing linear polymers of 7000-12000 D-glucose units. Cellulose constitutes about 41-43% of the plant (Jenkins et al., 1996a; Milne et al., 1990). Next in abundance is hemicellulose, which is around 20% in deciduous trees, but near 30% in conifers. This polysaccharide is formed by 100-200 monomers of glucose, mannose, galatose, xylose and arabinose (Parham and Gray, 1984; Simoneit, 2002). Lignin is the third component at around 27% in coniferous wood vs 23% in deciduous trees. It is a complex biopolymer with the main units derived from *p*-coumaryl, coniferyl and sinapyl alcohols (Rogge et al., 1998; Schultz and Taylor, 1989; Simoneit, 1993). These three components play an important role in emission production from biomass burning. Biofuels may also be composed, in lower proportions, of lipids, proteins, hydrocarbon components, simple sugars, starches, ash and other compounds (Jenkins et al., 1998; Sjöström, 1993).

1.1.1.2 Burning or Combustion process

Combustion of the individual fuel elements goes through a sequence of stages, each with different chemical and physical processes that result in different emissions. According to Jenkins et al. (1998) burning is a combination of reactants such as fuels, water, and air; reacting globally to produce some products of burning or emissions. The combustion or burning characteristics may show wide variation due to the type of fuel, the characteristics of combustion facility, dilution techniques used, sampling procedures, burning rate and the moisture content of the fuel (Fine et al., 2004b; Kowalczk et al., 1981; Lipsky and Robinson, 2006; Wardoyo et al., 2006).

The wood combustion process can be summarised as follows. With increasing temperature, the wood constituents begin to hydrolyse, oxidise, dehydrate and finally end up by pyrolysis (Simoneit, 2002). On the other hand, the process can be divided into three different phases: ignition, flaming and smouldering. Ignition is the heat absorbing phase of combustion where heat is applied to fuel, resulting in vaporisation of water and volatile combustible substances providing the gases that sustain flames in the next phase of combustion. Flaming is a phase of combustion where heat is released. This phase is the most efficient phase of combustion, producing the least amount of smoke per unit of fuel

consumed. The products of flaming combustion are primarily carbon dioxide and water vapour. Finally smouldering is the least efficient phase of combustion and produces more smoke. This phase does not present flame, and is associated with conditions where oxygen is limited, either by charing of fuels (particularly those with large surface to volume ratios) or by tightly packed fuels like duff and organic soils or in wet fuels.

1.1.1.3 Biomass burning process

Thermal degradation begins with a distillation step, in other words, with the release of water and volatiles species. The next step is pyrolysis, when thermal cracking of the fuel molecules occurs. This results in the formation of char with high carbon content, tar with intermediate molecular weight and volatile compounds in the form of a flammable white smoke. Above 180ºC, the process becomes exothermic, and at 530ºC, glowing combustion releases a complex mixture of tar and gaseous products, which form a flammable mixture when diluted with an oxydising atmosphere. This mixture ignites, forming a flaming combustion. This process converts the complex mixture of substances emitted during pyrolysis to simple molecules, particularly CO_2, H_2O, NO, N_2O, N_2, and SO_2 (Lobert and Warnatz, 1996; Yokelson et al., 1996, 1997). Depending on the interaction between chemical kinetics and physical dynamics in the flame, intermediate products, such as CO, CH_4, H_2, C_2H_4, C_2H_2, PAH, and soot particles, are also released during this stage. Smouldering phase begins after flaming combustion ends and when most volatiles have been released from the near-surface region of the fuel. At this lower-temperature (<580ºC) a large amounts of incompletely oxidised pyrolysis products are emitted (Lobert et al., 1991; Yokelson et al., 1997). The amount of substances emitted from a given fire and their relative proportions are thus determined, to a large extent, by the ratio of flaming to smouldering combustion. It is this proportion, often expressed as ‘‘combustion efficiency’’ (i.e., the ratio between CO_2 and the sum of all carbon species emitted), which has been used as an effective predictor for the composition of smoke gas emissions resulting from biomass fires (Ward et al., 1992).

1.1.2 Biomass burning: Emissions

Biomass burning emissions consist of a wide range of gaseous compounds and particulate matter. Biomass burning is known to be a source of carbon dioxide (CO_2),

methane (CH_4) and nitrous oxide (N_2O). Beyond that, it is a considerable source of chemically active gases such as nitric oxide (NO), carbon monoxide (CO) and volatile organic compounds (VOC).

It is well demonstrated that independently of fuel type, approximately 90% of the carbon released during biomass burning is oxidised to CO_2 or CO, and less than 5% of the carbon is released as particulate matter (e.g., Alves et al., 2011a; Andreae et al., 1998; Ferek et al., 1998; Ward et al., 1992).

The particles generated by biomass burning have three main components: particulate organic matter (POM) (~80%), trace inorganic species (~12–15%) and black carbon (i.e., soot) (~5–9%) (Reid et al., 2005).

1.1.2.1 Volatile organic compounds

Gaseous compounds can be separated in primary and secondary emissions products. During a low temperature phase (< 100ºC) the polyssaccharides and functional groups of hemicelluloses and lignin decompose. In this fire stage, methanol, light aldehydes, formic and acetic acid are the dominant emissions (Marutzky, 1991 cited by Kopmann et al., 2005). Above 220ºC the polymer structure of the wood is decomposed. In this stage, about 80% of the material is thermally decomposed and a large amount of gaseous compounds is emitted. The organic composition of the emissions is determined by the temperature and the rate of temperature increase. At temperatures of 250–500ºC methane, aldehydes, methanol, furanes and aromatic compounds such as benzene, toluene, ethyl benzene and phenol are emitted. The duration of this phase increases with the raise of the moisture content and the increasing amount of fuel material. The emitted gases, mostly oxygenated compounds, will be burnt more or less completely in the presence of oxygen leading to the formation of stable volatile organic compounds. During the flaming phase of a fire, the gaseous compounds are oxidised further in radical reaction chains that are, to some extent, similar to the VOC chemistry in the troposphere. In flames with oxygen excess the reactions are initiated by OH radicals; in flames with oxygen deficiency chemical reactions are initiated by the H radical. In the later situation, synthesis reactions are observed due to high concentrations of methyl radicals. These reactions result in hydrocarbons with higher molecular weight. Aromatic compounds are formed by chemical reaction in the flames and aliphatic compounds are added and cyclisised to form aromatics.

The amount of aromatic compounds is determined by the amount of aromatic precursors in the fuel material and by the flame temperatures. The ratio of the primary emitted aromatic compounds to the secondary formed is not yet known. Oxygenated aliphatic compounds are typically C_1- or C_2-hydrocarbons. This is due to the high rate coefficients for the oxidation of alkyl radicals with more than two carbon atoms. They decompose rapidly by the elimination of an alkene. The emission of oxygenated compounds depends greatly on the pyrolysis temperature, with maximum emission occuring at 350ºC. More than 50% of the emitted aldehydes are formaldehyde and acetaldehyde (Nussbaumer, 1989 cited by Kopmann et al., 2005). The use of moist fuel material increases the amount of emitted aldehydes.

In the smouldering phase the formation rate of volatile organic compounds is low. But, since there is no flame, there is little subsequent loss leading to a relatively high emission rates of organic compounds in this stage of the fire. The predominant emitted compound is carbon monoxide. Since the emission rates of all products of incomplete combustion emission tend to be correlated (e.g., Ferek et al., 1998), CO is often taken as a surrogate for hydrocarbons and particulate carbon (Kopmann et al., 2005).

1.1.2.2 Particulate organic material

The majority of particles resulting from biomass burning were reported to be less than 2.5 µm in diameter (Ferge et al., 2005; Hedberg et al., 2002; Hueglin et al., 1997).

Since the organic fraction of smoke particles is composed of unburned fuel components and the products of partial combustion, the bulk of the wood smoke organic fraction is likely to be composed of compounds structurally related to the thermally decomposed products of these wood components (Gao et al., 2003). The most common are carbohydrates (predominately levoglucosan) accounting 7–14% of fresh smoke particle mass (Fraser and Lakshmanan, 2000; Gao et al., 2003). Levoglucosan alone can account for 5% of particle mass (Graham et al., 2002; Hornig et al., 1985; Puxbaum et al., 2007; Simoneit et al., 2004). Acetic acid, acetone, phenols, and water result from the levoglucosan pyrolysis, during the combustion process. Methoxyphenols have been found in similar concentrations in wood smoke (Hawthorne et al., 1989). Aldehydes are also present. Less than one half of water soluble organic component of smoke particles are thought to be organic acids with the remainder being indeterminate or neutral, such as

alcohols (Gao et al., 2003; Graham et al., 2002; Mayol-Bracero et al., 2002; Mazurek et al., 1991). The organic acids are present in fresh smoke particles such as formate, acetate, and oxalate, typically make up <1% of total particle mass each (Ferek et al., 1998; Yamasoe et al., 2000). With new analytical techniques progress it was possible to identify gluconate as the dominant acid (Gao et al., 2003). Also present in trace quantities (on the order of <5% of total mass) are miscellaneous alcohols and sugars. Through Gas Chromatography - Mass Spectrometry (GC–MS) studies, aliphatics, polycyclic aromatic hydrocarbons (PAH), esters and alkanols have also been observed (e.g., Fang et al., 1999; Simoneit et al., 1996). On a similar magnitude as the acids, straight chain *n*-alkanes with carbon numbers on the order of 24–34 are prevalent. Fang et al. (1999) showed that for such species, carbon numbers on the order of 29–31 are favoured. Similar studies have shown that PAHs (the nuclei on which particles form) make up less than 1% of smoke particle mass (Jenkins et al., 1996b; Kamens et al., 1988; Pettersson et al., 2011).

1.1.2.3 Trace inorganic species

A large amount of information is available in the literature because identification and quantification techniques of tracer inorganic species are accessible and widely used. Inorganic elements such as Na, Mg, Si, S, Cl, K, Ca, and Fe were commonly found from biomass burning (Alves et al., 2010; Andreae et al. 1998; Cachier et al. 1995; Chaiyo et al., 2011; Ferek et al. 1998; Li et al., 2003; Maenhaut et al. 1996; Yamasoe et al., 2000).

Alkali earths and halides tend to dominate the inorganic species, both potassium and chloride account for 2–5% of fine particle mass. It has been often suggested that they are likely in the form of potassium chloride in the core of smoke particles with black carbon (e.g., Pósfai et al., 2003). Sulphur in the form of sulphate is also present in ~1% of fine particle mass. Despite being a small part of the mass particles (~< 10%), trace inorganic species analysis play an important role in biomass burning particle chemistry. Comparison of emissions showed significant composition differences between the various combustion equipments types, especially when comparing old-type residential appliances versus modern woodstoves and boilers with higher combustion efficiency. In complete combustion, the emissions are enriched in inorganic ash particles, such as alkali salts of potassium. Particles generated by low combustion temperatures or incomplete combustion

are characterised by a low content of inorganic constituents and a much higher organic carbon content (Bølling et al., 2009; Boman et al., 2004).

1.1.2.4 Black carbon or soot

Soot is formed from gaseous hydrocarbon fragments, at high temperature in the flames, normally in areas with insufficient air, and is often considered approximated as formed by black or elemental carbon. The soot chemical composition consists of solid carbon with a graphitic-like structure. Soot formation starts during volatilisation and combustion of organics when hydrocarbon fragments leave the biomass particles. These fragments then crack into smaller pieces and react with other fragments and surrounding gases to form aromatic rings. These ring structures are thought to add alkyl groups, developing into PAH. Thereafter, the particles grow by agglomeration. The resulting soot particles are thus composed of agglomerates of smaller spherical particles (Bäfver, 2008; Bockhorn, 1994).

1.2 Objectives

In Portugal and other Mediterranean countries, there is a lack of data on emission factors from biomass burning. Additionally in Southern Europe, the detailed chemical characterisation of biomass burning emissions has not been made so far. Emission inventories and source apportionment, photochemistry and climate change models, all have been using default values obtained for USA (e.g. Fine et al., 2004a,b), mid-European Alpine regions (Schmidl et al., 2008), or Scandinavian (Hedberg et al., 2002; Johansson et al., 2004) biofuel combustion, uncommon in Southern Europe. Thus, it is desirable to use more representative and specific locally acquired data. This study deals with the characterisation and quantification of the contribution of biomass combustion sources to atmospheric trace gases and aerosol concentrations more representative of the Portuguese reality.

This study encompassed the following parts: characterisation of particulate matter with aerodynamic diameter below 10 μm (PM_{10}) from modern woodstove combustion (Chapter 2); rate emissions and chemical composition of the particulate matter with aerodynamic diameter below 2.5 μm ($PM_{2.5}$) from fireplace and typical cast iron

woodstove combustion (Chapters 3 and 4); emission from the field burning of garden and agriculture residues (Chapter 5); characterisation of emissions from experimental wildland fires (Chapters 6 and 7); and finally a national inventory of emissions that are released from residential wood combustion (RWC) in Portugal (Chapter 8).

1.3 Experimental work

1.3.1 Biomass selection

The Portuguese forest is an old ecosystem represented by a wide variety of species (Figure 1.1). The north coast of the country presents a higher abundance of maritime pine, eucalypt and Golden wattle. The northern inland regions are characterised by the presence of Portuguese oak and Portuguese chestnut, while the south is mainly covered by Cork oak and Holm oak. The species distribution is determined by the type soil, water availability and climate in each region. Portugal has one of the largest forested areas of Europe, covering 35.8% of the territory, which corresponds to 3.3 million hectares (*Direcção Nacional de Gestão Florestal*).

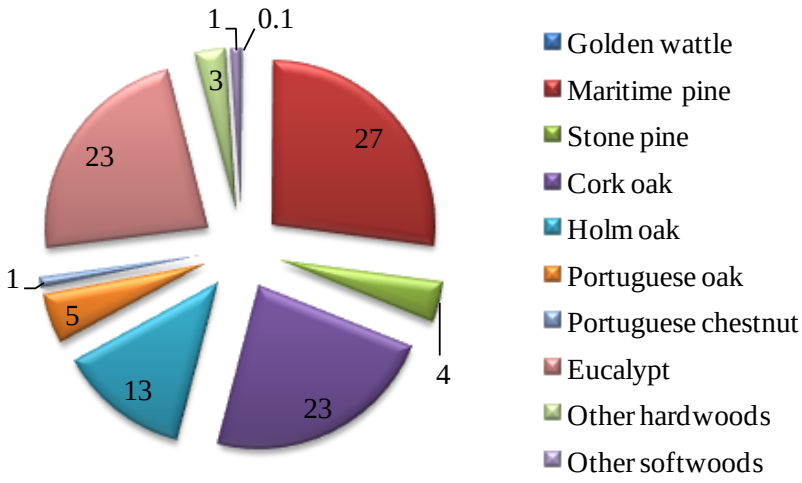


Figure 1.1 Forest distribution in Portugal (%).

The main criterion for biomass selection for the experimental work was based on the availability of tree species in the Portuguese forest, which represents the most commonly used biofuels in domestic combustion. Maritime pine (*Pinus pinaster*), eucalypt (*Eucalyptus globulus*), cork oak (*Quercus suber*) and golden wattle (*Acacia longifolia*)

(Figure 1.2A) were the species selected for the combustion experiments in the modern woodstove of Vienna University of Technology (Chapter 2). For the traditional cast iron woodstove and brick fireplace tests, carried out at University of Aveiro, maritime pine (*Pinus pinaster*), eucalypt (*Eucalyptus globulus*), cork oak (*Quercus suber*), olive (*Olea europea*), Portuguese oak (*Quercus faginea*), Holm oak (*Quercus ilex rotundifolia*) and golden wattle (*Acacia longifolia*) (Figure 1.2A) were the species used. In addition, biomass briquettes made of wastes from forest cleaning activities and/or wastes from local wood processing industries, common in home heating nowadays, were also studied and evaluated (Chapters 3 and 4).

Figure 1.2 Biofuels used for the characterisation of combustion emissions in this study.

The characterisation of emissions from the field burning of garden and agriculture residues, presented in Chapter 5, relates to three types of biofuels: dried potato branches and leaves (*Solanim tuberasum*), weed vegetation (*Trifolium campestre, Echium plantagineum, Ornithopus perpusillus, Solanum nigrum,* etc.), and stalks from collard greens (*Brassica oleracea*) and pruned green leafy-twigs together with thin branches from garden trees (Figure 1.2B). Chapters 6 and 7 present the characterisation of experimental fires in a shrub-dominated forest. The vegetation cover was composed by some isolated pine trees (*Pinus pinaster*) and a continuous mass of dwarf Spanish heath (*Erica umbellata*), Spanish heather (*Erica australis*) and prickled broom (*Chamaespartium tridentatum* or *Genista tridentata*) (Figure 1.2C).

1.3.2 Laboratory and field facilities

1.3.2.1 Laboratory facilities: Combustion equipments

The domestic combustion equipments used in this study are divided into the following groups:

- Modern woodstove (Chapter 2)
- Traditional cast iron woodstove (Chapters 3 and 4)
- Traditional brick fireplace (Chapters 3 and 4)

Modern woodstove: characterisation

At the Vienna University of Technology, a sophisticated “chimney type” logwood stove with a nominal power output of 6 kW was used. The woodstove is of the model Fox, manufactured by the Austrian company Rika. This type of equipment is commonly found in Austria, Hungary, Germany, Switzerland, Bohemia, Northern Italy and Scandinavia, but is gradually conquering the market in Southern Europe. Combustion air enters the burning chamber (28x25x25cm) through a grate in the bottom (primary air) and a slit in the back wall (secondary air). Exhaust gases are redirected 2 times prior to entering the chimney. Airflow is controlled manually via a rotary knob connected to a valve system that adjusts both primary and secondary combustion air flow. The stove temperature (at the centre of the combustion chamber) and its exit flue gas characteristics, such as temperature, O_2, CO_2, CO, NO, and total hydrocarbons, were monitored continuously at the exit of the stove chimney at 2.0 m above the exit of the stove combustion chamber. The temperature was

monitored using K-type thermocouples. The measurement principles of the gas analysers were non-dispersive infrared (CO and CO_2), paramagnetic (O_2), chemiluminescence (NO) and flame ionisation (total hydrocarbons expressed as methane-equivalents). Each gas analyser was calibrated with appropriate gas on zero and span points. Dilution factors used in the dilution tunnel ranged from 1:10 to 1:15, enabling temperatures at the particulate matter sampling port only a few degrees Celsius higher than ambient values. The dimensions of the dilution tunnel were 1 m in length and 0.2 m in width resulting in an average residence time of 50 seconds at a flow rate of 2.3 m^3 h^{-1}. PM_{10} was sampled from the dilution tunnel with a low volume sampling head (Digitel AG, Switzerland) working on a one-stage impactor principle at a flow of 2.3 m^3 h^{-1} , which was further distributed to 47 mm diameter aluminium filter holders (Pall Life Sciences). The filter holders were equipped with six quartz fibre filters (Tissuquartz, Pall 205 Life Sciences) and two mixed cellulose ester filters (GN-4 Metricel, Pall Life Sciences). The sampling flow through quartz fibre filters was set to 0.33 m^3 h^{-1} per filter, while the flow through cellulose filters was 0.165 m^3 h^{-1}. This was necessary because of the high pressure drop of cellulose filters. The flows through both sampling lines were regulated with mass flow controllers (Bronkhorst) after drying the diluted flue gas with activated silica to refer to dry conditions (Fernandes et al., 2011; Schmidl et al., 2008, 2011) (Figure 1.3).

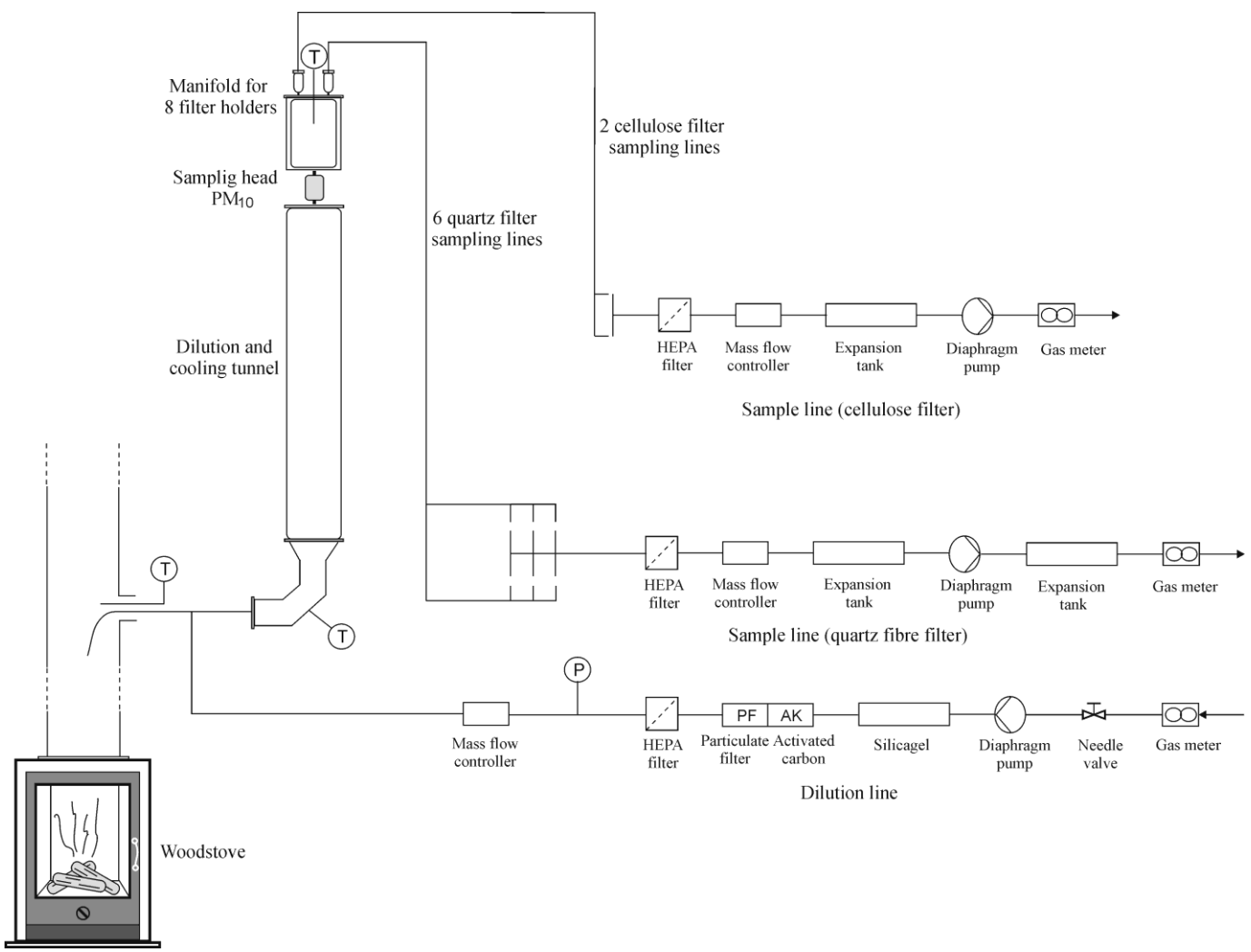


Figure 1.3 Schematic representation of the combustion facility, including the modern woodstove, of Vienna University of Technology.

Traditional cast iron woodstove and brick fireplace: characterisation

At the University of Aveiro, the combustion tests were conducted in a traditional cast iron woodstove and in a Portuguese brick fireplace of the type used in Portugal for domestic heating purposes.

The woodstove used is of the model Sahara, manufactured by the Portuguese company Solzaima using stainless steel, with the front panel and grate made in iron cast and a combustion chamber with a volume of around 0.09 m^3 (Figure 1.4). The stove is charged with batches of wood over the grate in the combustion chamber. The air enters the combustion chamber through a regulation device located in the down door, which also supports the hopper for collecting the bottom ashes, located below the grate. The driving force for the air flow rate throughout the combustion chamber is the natural convection resulting from the up flowing stream of combustion hot flue gases through the vertical exhaust duct (chimney) (Tarelho et al., 2011).

The fireplace used has a combustion chamber with a volume of around 0.15 m^3 (Figure 1.5). The wood logs are supported by a fixed grate and, in this case, there is no hopper for collecting the bottom ashes. In this combustion appliance there is no device for regulating the combustion air flow. The air enters the combustion chamber through the front opening and flows below and above the fixed bed of burning biomass. The driving force for the air flow rate throughout the combustion chamber is the natural convection resulting from the up flowing column of the hot combustion flue gases throughout the chimney.

Both burning appliances were equipped with a chimney with 0.2 m internal diameter, and 3.3 m height in the case of the woodstove, and 2.7 m height in the case of the fireplace, in order to have the chimney exit at the same height (B in Figures 1.4 and 1.5). In the case of the woodstove, the first section of the exhaust duct above the stove exit was thermally insulated (with Cerablanket, 128 kg/m^3, 0.025 m, 0.23 W/m/K), due to operation safety reasons (Tarelho et al., 2011)

The woodstove was equipped with a combustion grate connected to a weight sensor (load cell DSEUROPE Model 535QD-A5), in order to get continuous monitoring of the fuel mass in the combustion chamber grate (H in Figure 1.4).

The gas flow rate through the combustion chamber was accessed by using: i) a mass flow meter (Kurz, Model: 500-2.0-P 40) for combustion air flow rate entering the

combustion chamber, in the woodstove case (I in Figure 1.4), and ii) a Pitot tube located in the chimney and respective pressure sensor, making part of a Testo AG 808 equipment, in the fireplace case.

The combustion flue gas temperature was monitored using K-type thermocouples at several locations along the facilities, namely, in the woodstove under the fixed bed of fuel, at the central region of the combustion chamber and along the chimney height (1, 2, 3 and 4 in Figures 1.4 and 1.5).

The combustion flue gas composition was characterised on-line by using a gas sampling and analysing system which comprises a set of on-line analysers, namely: O_2 (paramagnetic, ADC model O_2-700 with a Servomex Module), CO_2 and CO (non-dispersive infrared, Environnement, MIR 9000) (G in Figures 1.4 and 1.5).

For O_2, CO_2 and CO analysis, the combustion flue gas sampling and analysing system includes a water-cooled sampling probe, a set of gas conditioning and distribution units, and the on-line gas analysers (F in Figures 1.4 and 1.5). The combustion flue gas was sampled at a flow rate of 2 L min^{-1} (atmospheric temperature and pressure) at the exit of the chimney; the probe tip was located at the axial line of the chimney. The sampling probe was equipped with an external circulating quenching water sleeve, an ice-cooled particle gas filter, a K-type thermocouple and a Cerablanket plug at the tip for exhaust gas particle filtering. The gas conditioning and distribution units include gas flow meters, a filtering system for particulate removal, a gas sampling pump, a heat exchanger immersed in an ice bath for gas quenching and water vapour removal, and a gas distribution unit. The gas distribution unit consisted of pneumatic circuits that permit to deliver calibration gas, purge gas and sample gas to the analysers.

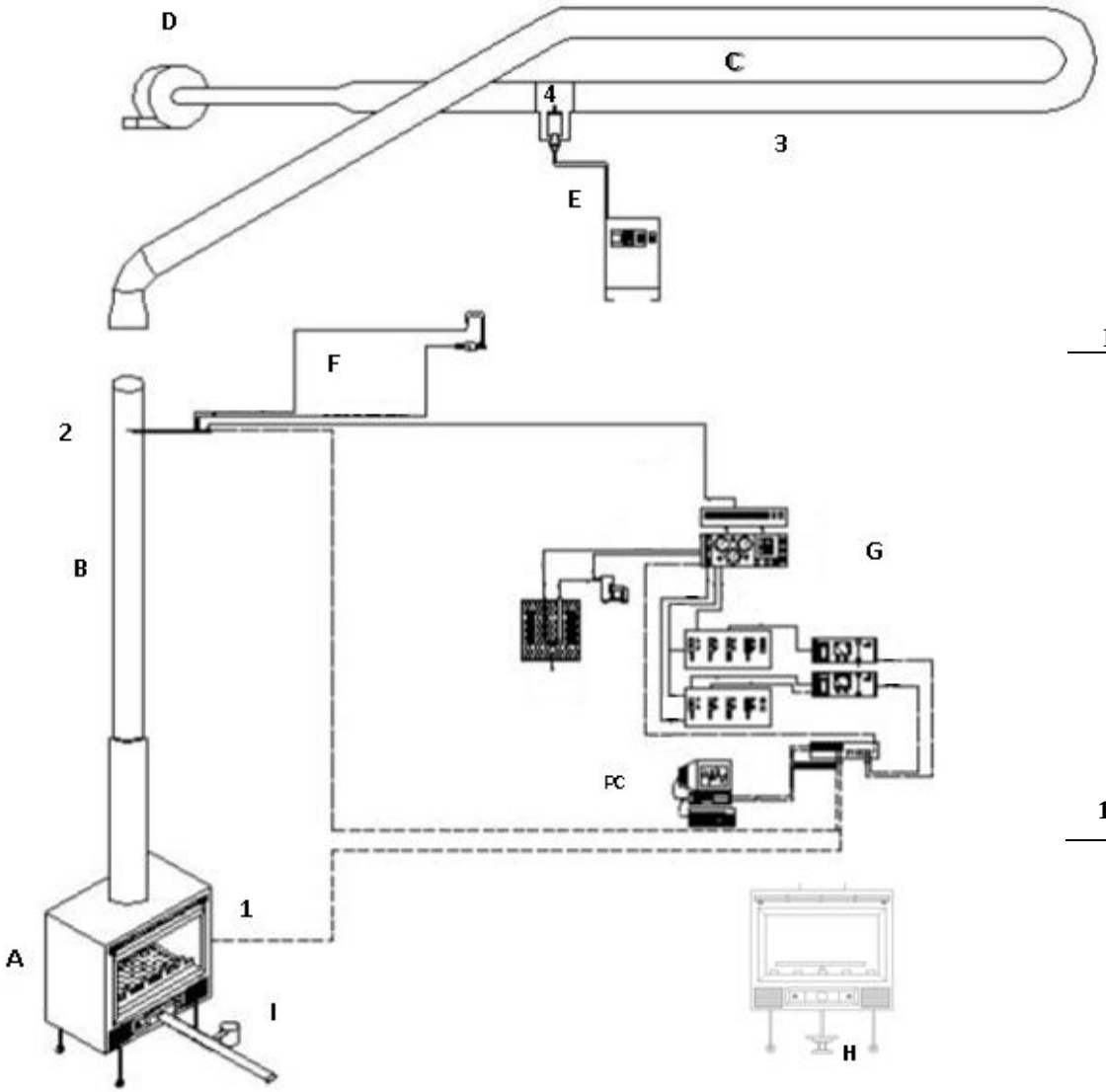
For total hydrocarbons (THC) analysis (expressed as CH_4), a heated probe and sampling line (at 190ºC) was used for gas sampling. The sampling probe was located at a height of 2.8 m in the chimney. The flue gas sample was directly analysed by FID. The sampling probe tip was located at the axial line of the chimney and a Cerablanket plug is putted at the tip probe for combustion flue gas particle filtering (Tarelho et al., 2011).

The operation and monitoring of the entire system was performed by a computer based control and data acquisition hardware and software system.

For particulate matter ($PM_{2.5}$) sampling, a dilution tunnel and respective ancillary equipment, was installed downstream of the chimney in order to dilute the combustion flue

gas exiting the chimney. The dilution tunnel used had 0.20 m internal diameter, and 11 m length. The dilution ratios applied to the flue gases from the woodstove were around 25:1. In the case of the fireplace, 4- to 5-times dilution ratios were applied. The particulate matter sampling point was located at 10 m downstream the dilution tunnel entrance. The sampling train included a specific sampling head ($PM_{2.5}$), a pump, and a control and data acquisition system, all part of a TCR TECORA (model 2.004.01) instrument, operating at a flow of 2.3 m^3 h^{-1} (E in Figures 1.4 and 1.5). A K-type thermocouple was placed near the sampling head to measure the temperature of the flue gas (combustion flue gas from the stove/fireplace diluted with atmospheric air) (4 in Figures 1.4 and 1.5). The temperature in the particle sampling point was in the range 25–35°C, and the relative pressure was maintained typically at 10 mm H_2O below the atmospheric pressure. The gas flow velocity was around 6.3 m s^{-1}.

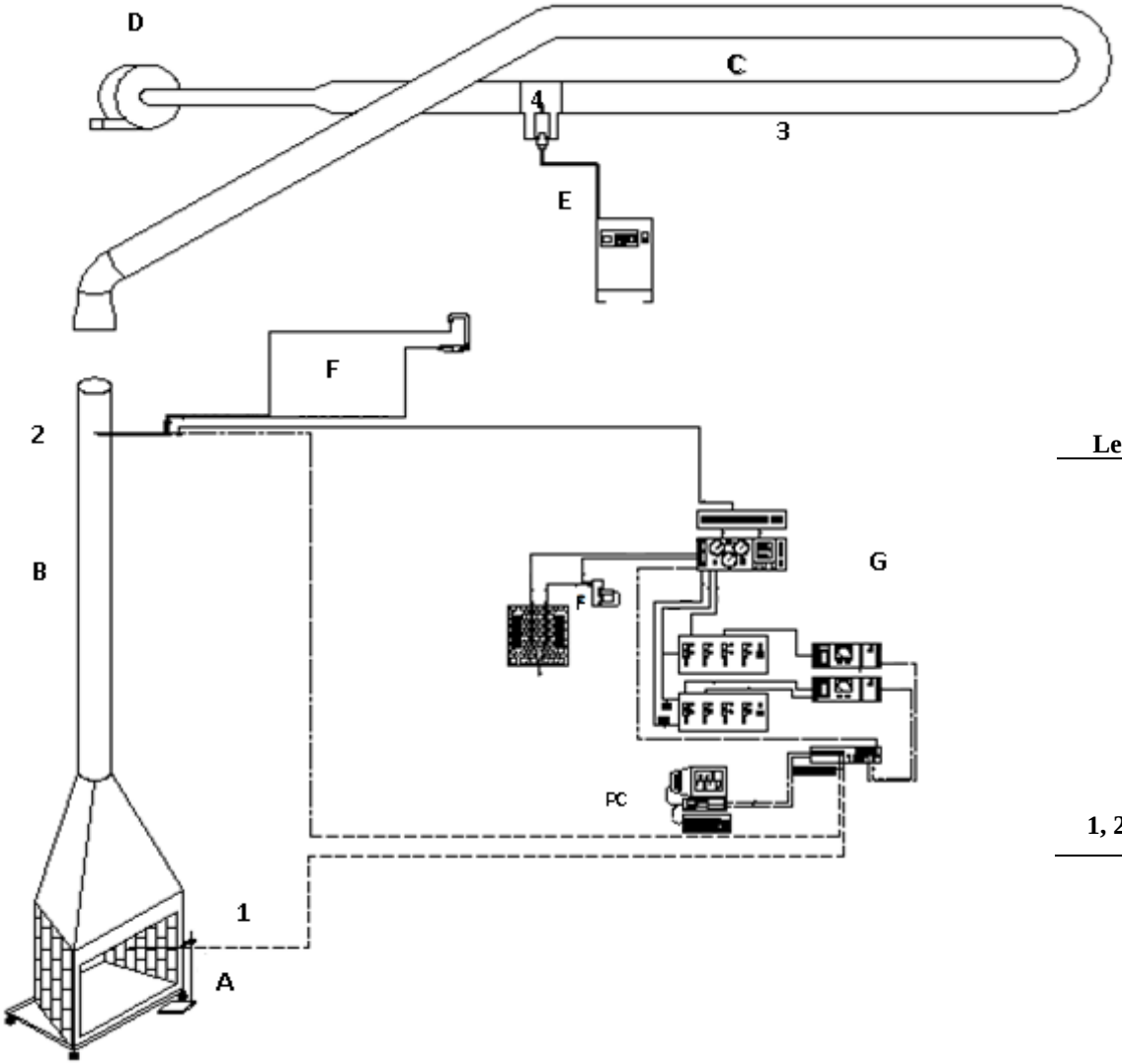
The volumetric gas flow rate throughout the tunnel, and respective combustion gas dilution ratio were calculated from the mean gas velocity in the cross section of the dilution tunnel. This mean gas velocity was estimated based on the differential pressure monitoring using a Pitot tube and respective pressure sensor, making part of Testo AG 808 equipment, and a K-type thermocouple (Fernandes et al., 2011; Tarelho et al., 2011).



Legend:

A	Woodstove
B	Chimney
C	Dilution tunnel
D	Blower
E	Particle sampling system
F	Cooling system for gas sampling probe
G	Gas analysers, data acquisition and system control
H	Weight sensor
I	Mass flow meter
1, 2, 3 e 4	Thermocouples

Figure 1.4 Schematic representation of the traditional woodstove of University of Aveiro (Fernandes, 2009).



Legend:

A	Fireplace
B	Chimney
C	Dilution tunnel
D	Blower
E	Particle sampling system
F	Cooling system for gas sampling probe
G	Gas analysers, data acquisition and system control
1, 2, 3 e 4	Thermocouples

Figure 1.5 Schematic representation of the traditional brick fireplace of University of Aveiro (Fernandes, 2009).

1.3.2.2 Field facilities

In the characterisation of garden and agriculture residues field burning (Chapter 5) and in experimental wildland fires (Chapters 6 and 7), a tripod high-volume sampler/impactor (Tisch Environmental Inc.) operating at a flow of 1.13 m^3 min^{-1} was used to collect sequentially, on pre-baked quartz fibre filters, large coarse ($PM_{>10}$), coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$) smoke particles. The impaction system for capturing $PM_{>10}$ was designed at the University of Aveiro in accordance with the Marple and Rubow's theory (1986). A Tisch impaction plate TE-231 F was used to separate particles smaller than 2.5 µm. Quartz filters used as impaction substrates have been shown to minimise particle bounce without affecting the cutpoint of the impactor (Chang et al., 2001).

In parallel and simultaneously, Tedlar bags previously flushed with N_2 were used for the collection of gas samples. Pre-removal of water vapour from the air stream was carried out in a U glass tube filled with glass spheres, immersed in an ice bath. In addition, and previously to the water vapour removal, the air stream was filtered through a 4.7 mm quartz filter to remove particles before passing to the collection system, which also contained a Teflon-lined diaphragm pump connected to a needle valve and a calibrated rotameter operating at a flow rate of 1 L min^{-1}. After sampling, the bags were stored in opaque containers in order to minimise U.V. radiation of the samples. The time period between sampling and analysis was reduced to a few hours to avoid secondary reactions. A schematic diagram of the open burning experiments is presented in Figure 1.6.

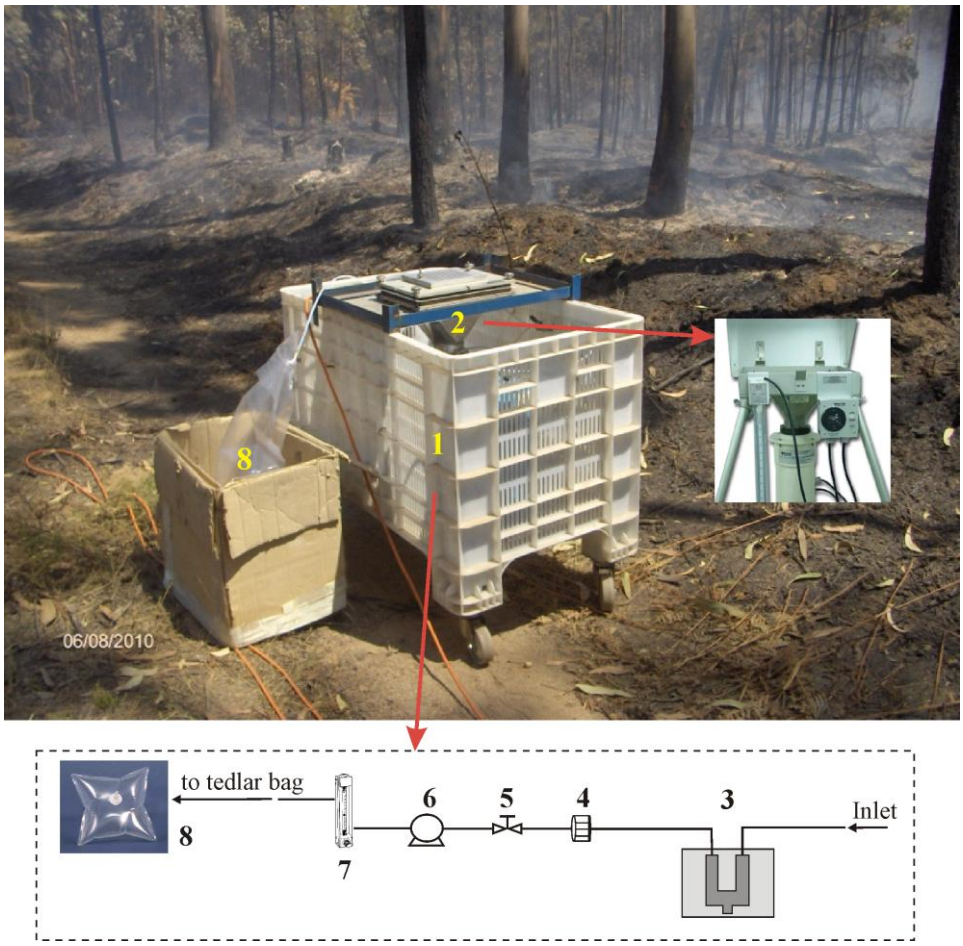


Figure 1.6 Schematic diagram of the experimental setup.
1) Portable box; 2) PM sampler; 3) U-shaped tube filled with small glass balls in an ice bath to remove water vapour; 4) Filter holder (Ø= 47 mm) to remove particles from the air stream; 5) Needle valve; 6) Teflon pump; 7) Rotameter; 8) Tedlar bag.

1.3.3 Filters treatment

In the field work, quartz fibre filters have been used as particle collection substrates. According fine particles ($PM_{2.5}$) were collected over filters 20.3 x 25.4 cm (Whatman QM-A); coarse ($PM_{2.5-10}$) and large coarse ($PM_{>10}$) particles were collected over the same type of quartz filter, adapted to the sample plate holder of the two-stage cascade impactor, by cutting the original rectangular quartz filters into strips. In laboratory combustion tests filters with a 47 mm diameter were used (Tissuquartz, Pall Life Sciences and GN-4 Metricel, Pall Life Sciences).

All filters used in this work (except cellulose filters) were wrapped in aluminium foil and pre-baked at 500ºC or 600ºC for 6 hours to eliminate organic contaminants. The filters

were placed in an air-conditioned room or in a desiccator to stabilise without hydration or contamination. Before and after sampling the gravimetric analysis was performed with a microbalance Sartorius M5P with range up to 1 g reading to ± 0.5 µg in Vienna University of Technology and with a microbalance Mettler Toledo AG245 (readability-0.1mg/0.01mg) in University of Aveiro. Filter weight was obtained from the average of three measurements, when the variations were less than 5%.

1.3.4 Organic carbon and elemental carbon measurement

The carbonaceous content (EC and OC) of particulate matter was analysed by a thermal-optical technique. Two 9 mm diameter filter punches, in the case of $PM_{2.5}$ samples, or strips representing 1/20 of the total area, in the case of $PM_{2.5–10}$ samples, were used in each analytical run. For each filter, two replicate analyses were done. Controlled heating in anoxic conditions was performed to separate OC into two fractions of increasing volatility. The first fraction corresponds to the volatilisation at T<200°C of lower molecular weight organics (OC1). The second fraction is related to decomposition and oxidation of higher molecular weight species at temperatures ranging from 150 to 600°C (OC2). The last fraction of OC is identified by transmittance and corresponds to pyrolysed organic carbon (PC) produced in the previous heating steps. The OC and EC separation was achieved by the previous heating of the filter punches under an inert atmosphere to evaporate the OC fraction. The remaining fraction is sequentially evaporated/burnt under a gas flow containing O_2. This last carbon fraction contains initial EC plus OC that has pyrolysed during heating under an inert atmosphere. The interference between PC and EC can be controlled by continuous evaluation of the blackening of the filter using a laser beam and a photodetector measuring the filter light transmittance. This procedure was originally developed by Pio et al (1994) and Carvalho et al (2006) and was adapted by Alves et al (2011b).

1.3.5 Anhydrosugars

In the case of samples from the Austrian combustion facility, particulate matter on each filter piece was extracted with Milli-Q water through ultrasonic agitation. After centrifugation the aqueous phase was analysed by high performance liquid chromatography (HPLC) with an electrochemical detector (Dionex ED40, pulsed

amperometry with gold working electrode). Quantification is based on the use of levoglucosan as an external standard. The method also yields results for some other sugars including fructose, galactosan, glucose and mannosan. (Caseiro et al., 2007; Simoneit et al., 1998, 2004). In the case of samples from the Portuguese combustion facility, anhydrosugars were analysed by GC-MS after solvent extraction and derivatisation, as described in section 1.3.11.

1.3.6 Cellulose

After elution with a 0.05 M citric acid solution (pH = 4.8), extraction in an ultrasonic bath and saccharification to glucose through the action of two enzymes (a *Trichoderma reesei* cellulase and an *Aspergillus Niger* cellobiase), cellulose is determined photometrically using a modified test-combination (by Boehringer Mannheim GmbH / R-Biopharm).

The glucose determination involves two steps. First it is phosphorylated to glucose-6-phosphate by the enzyme hexokinase (HK) transferring phosphate from ATP:

$$G + ATP + HK \rightarrow G\text{-}6\text{-}P + ADP \quad (1)$$

In the second step, G-6-P is oxidised by $NADP^+$ in the presence of the enzyme G-6-P dehydrogenase, with the formation of NADPH:

$$G\text{-}6\text{-}P + NADP^+ + G\text{-}6\text{-}P\text{-}DH \rightarrow \text{gluconate-}6\text{-}P + NADPH + H^+ \quad (2)$$

The amount of NADPH formed is in direct relation to the amount of glucose, but as there is already some colour in the solution before this second step takes place, it is necessary to measure the absorbance before and after step (2) to quantify the yield of NADPH. The NADPH absorbs at 340 nm. An apparent absorption coefficient is calculated relating the difference in absorbance, ΔA, to the amount of glucose taken. (Kunit et al., 1996, 2003; Sánchez-Ochoa et al., 2007).

1.3.7 Humic-like substances (HULIS)

Particulate matter, on filters from the combustion facility of Vienna, is first extracted with water and then with diluted alkali. Pre-concentration and clean-up of these separate extracts is achieved by using solid phase extraction (SPE) with a size exclusion phase. This step is followed by a further clean-up step using an anion exchange column in a flow-injection system, and the organic material eluting is quantified by on-line total organic carbon (TOC) determination. Eluant solutions of approximately known pH are prepared by dilution of strong acid and strong base. Buffers are not used as the repeated injection of high-salt solutions into the TOC furnace because leads to rapid deterioration of the catalyst (Havers et al., 1998).

1.3.8 Soluble inorganic ions

For the determination of soluble inorganic ions, small parts of the filters were extracted with ultra pure Milli-Q water. Dionex AS14 and CS12 chromatographic columns with Dionex AG14 and CG12 guard columns coupled to Dionex AMMS II and Dionex CMMS III suppressors, have been used for anions and cations, respectively (Freitas et al., 2009).

1.3.9 Metals

Cellulose acetate filters from the combustion facility at Vienna were used for metal analyses by inductively coupled plasma optical emission spectrometry (ICP-OES) and X-ray fluorescence spectroscopy (XRF) (Schmidl et al., 2008). Metals from quartz fibre filters from the Aveiro combustion facilities were analysed by inductively coupled plasma mass spectrometry (ICP-MS), according to the methodology described in Chapter 4. Inducted neutron activation analysis (INAA) was the technique used for the determination of metals from the experimental wildland fires.

1.3.10 Radionuclides

Radionuclides in PM_{10} filters from the combustion facility of Vienna were measured by α-spectrometry after application of a sequential extraction and purification technique (Carvalho et al., 2007; Oliveira et al., 2006).

1.3.11 Organic speciation

1.3.11.1 Particulate matter extraction

The extraction is defined as a process to separate the constituents with analytical interest from a mixture by dissolving in a solvent where only those constituents are soluble.

In this work, the organic particulate material was extracted by refluxing dichloromethane (DCM) for 24 hours. During this process, the sample is placed in a glass balloon with solvent connected to a condenser. With the help of a heating blanket, the solvent remains in the boiling point without applying any external pressure. The condenser cools the solvent and the system keeps the balance (Figure 1.7). The laboratory equipment required to make this type of extraction is very simple. The liquid extraction of a solid matrix results in dilution of the sample in a large volume of solvent. It is recommended to concentrate the solvent using appropriate methods to reduce the volumes and, simultaneously, maintain unalterable the composition of the extracted matter extracted.

Figure 1.7 Extraction process by refluxing dichloromethane.

The extracts from Vienna combustion facility, from garden and agriculture residues field burning and forest fires obtained after refluxing, with approximately 300 mL of DCM, were first subjected to filtration and then concentration (Figure 1.8) until they reached a volume of 3 to 5 mL using a rotary evaporator (Laborata 4002 - Digital) with constant-temperature bath (nearly 33°C). Concerning samples from the woodstove and fireplace, after filtration, filter pieces were then extracted 3 times with methanol (75 mL for 10 min, each extraction) in an ultrasonic bath. Additional extraction with methanol was added to the procedure to increase the efficiency of extraction of additional polar

compounds. The efficiency increased from approximately 70% to more than 90%. The total organic extract (TOE) obtained was transferred to small vials and then subjected to a stream of nitrogen at low flow, to dry it up.

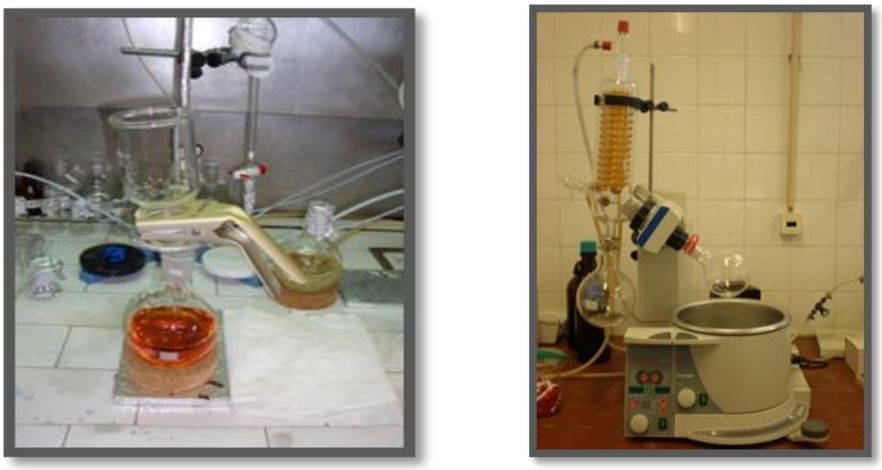


Figure 1.8 Filtration and concentration of the extracts.

1.3.11.2 Fractionation

The vials containing TOE were subjected to a fractionation procedure originally developed by Stephanou and Stratigakis (1993), Gogou et al. (1998) and adapted by Alves et al. (1999). This technique is a variant of the traditional column chromatography, relatively simple and easy to implement. It is commonly known as flash chromatography. The system includes a valve to control the supply of nitrogen, a glass balloon that serves as a reservoir for solvents and a glass column with the appropriate dimensions to place the adsorbent material.

This technique uses solvents of increasing polarity in order to separate different families of compounds present in TOE from the aerosol. Thus, the sample is placed inside a glass column (30×0.7 cm) in contact with 1.5 g of silica gel (3-6 mm, Panreac) with a high degree of polarity (activated at 150°C during 3 hours). The TOE is washed with different mixtures of solvents and is added to the silica column. The following solvents were used to elute the different compound classes: (1) 22.50 mL *n*-hexane (fraction 1, aliphatics); (2) 22.50 mL toluene–*n*-hexane (8.40:14.10) [fraction 2, polycyclic aromatic hydrocarbons (PAHs)]; (3) 22.50 mL *n*-hexane–dichloromethane (11.25:11.25) (fraction 3, carbonyl compounds); (4) 30.00 mL ethyl acetate–*n*-hexane (12.00:18.00) (fraction 4, *n*-

alkanols, sterols and other hydroxyl compounds); and (5) 30.00 mL solution of pure formic acid in methanol (4%, v/v) (fraction 5, acids and sugars). The different solvent mixtures are passed successively through the silica column aided by a nitrogen stream, resulting in five separate fractions (Figure 1.9). For each fractions collected in balloons the solvent was removed on the rotary evaporator, approximately up to 2 mL, maintaining the bath temperature at about 33 °C. Then, the resulting extracts were transferred to vials and dried under a nitrogen stream. Recovery efficiency tests for several compounds can be found elsewhere (Alves, 2001; Carvalho, 2003; Gogou et al., 1998, Oliveira et al., 2007).

Figure 1.9 Flash chromatography with silica gel and five separate fractions.

1.3.11.3 Derivatisation

Polar COOH and OH groups on which hydrogen bonding may be converted to relatively nonpolar groups on a relatively nonvolatile compound; the resultant product may be less polar, thus more volatile, allowing analysis by gas chromatography (Blau and Darbre, 1993; Evershed, 1993). Fractions 4 and 5, corresponding to alcohols, sterols and sugars/acids, respectively, are subjected to a derivatisation process, before the chromatographic analysis. Thus, both fractions were subjected to a silylation process. Silylation is one of the most used modes of derivatisation, due to the fact that there are a wide variety of chemical agents available. The *N*,*O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) has been widely used as a reagent for silylation, because its products are enough volatile, rarely interfering with the analyte peaks in the chromatograms. For GC-MS analysis, the addition of trimethylchlorosilane group (TMCS) to polar compounds gives

thermal and chemical stability, as well as an increase in volatility (Evershed, 1993). The silylation of fractions 4 and 5 was carried out by placing volumes of BSTFA:TMCS (99:1) (Supelco 33149-U) at a ratio of 1:1 and 1:2, respectively, in contact with the extract and solvent (pyridine) with subsequent heating to 70 °C for 3 hours in an oven.

1.3.11.4 GC-MS analysis

The analysis by GC-MS has been one of the most common means to identify organic compounds in atmospheric aerosol samples. This is mainly because GC can separate a very ample range of compounds on a single column, and the simple on-line coupling to mass spectrometry (usually electron-impact quadrupole) makes the compound identification rather easy.

In this work, the fractionated extracts were analysed with a GC model 6890, quadrupole MSD 5973 from Hewlett Packard and GC Trace Ultra, quadrupole DSQ II from Thermo Scientific both with a TRB-5MS 60 m×0.25 mm×0.25 μm column. Data were acquired in the electron impact (EI) mode (70 eV). The ovens temperature program was as follows: 60 °C (1 min); 60–150 °C (10 °C min^{-1}), 150–290 °C (5 °C min^{-1}), 290 °C (30 min) and using helium as carrier gas at 1.2 mL min^{-1}.

The GC-MS system was accurately calibrated using about 150 high purity individual compounds in different concentration levels with relative response factors determined individually for the majority of compounds. All samples and authentic standards were injected with two internal standards: tetracosane-D_{50} (Sigma-Aldrich) and 1-chlocohexadecane (Merck). Additionally, the EPA 8270 semi-volatile internal standard mix (Supelco), containing six deuterated compounds (1,4-dichlorobenzene-d_4, naphthalene-d_8, phenanthreme-d_{10}, chrysene-d_{12}, perylene-d_{12}), has been used for PAHs analysis. A detailed description of the analytical methodology, including recovery efficiency tests for several compounds, can be found in Alves and Pio (2005) and Oliveira et al. (2007). This methodology was previously tested in our laboratory (Alves 2001; Carvalho et al., 2003) and elsewhere (Gogou et al. 1998). Compound identification was based on comparison of resulting spectra with mass spectra libraries (Wiley 275 and NIST MS Search 2.0), co-injection with authentic standards and analysis of fragmentation patterns.

1.3.12 Gaseous compounds

The gas phase samples from field burning of garden and agriculture residues were analysed for CO_2 and CO using a non-dispersive infrared analyser (Environnment, MIR 9000). All gas samples from experimental wildland fires were examined for CO_2, CO, N_2O, NO, NO_2, SO_2, NH_3, CH_4, ethane, propene, acetylene and methanol using a Fourier transform infrared spectrometer, according to the methodology described in Chapter 7.

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CHAPTER 2

Chapter 2. Characterisation of PM_{10} emissions from woodstove combustion of common woods grown in Portugal

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Abstract

A series of source tests was performed to evaluate the chemical composition of particle emissions from the woodstove combustion of four prevalent Portuguese species of woods: Pinus pinaster (maritime pine), Eucalyptus globulus (eucalypts), Quercus suber (cork oak) and Acacia longifolia (golden wattle). Analyses included water-soluble ions, metals, radionuclides, organic and elemental carbon (OC and EC), humic-like substances (HULIS), cellulose and approximately l80 organic compounds. Particle (PM_{10}) emission factors from eucalypts and oak were higher than those from pine and acacia. The carbonaceous matter represented 44 to 63% of the particulate mass emitted during the combustion process, regardless of species burned. The major organic components of smoke particles, for all the wood species studied, with the exception of the golden wattle (0.07–1.9% w/w), were anhydrosugars (0.2–17% w/w). Conflicting with what was expected, only small amounts of cellulose were found in wood smoke. As for HULIS, average particle mass concentrations ranged from 1.5% to 3.0%. The golden wattle wood smoke presented much higher concentrations of ions and metal species than the emissions from the other wood types burning. The results of the analysis of radionuclides revealed that the ^{226}Ra was the naturally occurring radionuclide more enriched in PM_{10}. The chromatographically resolved organics included n-alkanes, n-alkenes, PAH, oxygenated

PAH, n-alkanals, ketones, n-alkanols, terpenoids, triterpenoids, phenolic compounds, phytosterols, alcohols, n-alkanoic acids, n-di-acids, unsaturated acids and alkyl ester acids.

Keywords: biomass burning, woodstove, PM_{10}, emissions, organic tracers, GC-MS.

2.1 Introduction

The radiative forcing of climate by atmospheric aerosols is believed to be similar in magnitude, but opposite in sign, to the global warming caused by the emissions of greenhouse gases (Chung and Seinfeld, 2002; Danny and Kaufmann, 2002). Nowadays fine particles and the associated organic compounds are also reason for concern because of their effects in human health (Naeher et al., 2007). In Europe, emissions from biomass combustion sources can contribute up to 80% of the atmospheric aerosol mass during winter (Puxbaum et al., 2007). In Portugal, it was estimated that around 390000 ton/year of wood are burned in fireplaces (Dias, 2002). Wood burning results in high levels of toxic air pollutants, perturbing the atmospheric chemistry (Levine, 2003). In Mediterranean countries, data on detailed emission factors from biomass burning are mostly inexistent. Emission inventories and source apportionment, photochemistry and climate change models, all use default values obtained for American (e.g. Fine et al., 2004a,b), Alpine (Schmidl et al., 2008a), or Scandinavian (Hedberg et al., 2002; Johansson et al., 2004) biofuel combustion, uncommon in Southern Europe. Thus, it is desirable to use more specific locally available data. This research is focused on meeting the need for detailed characterisation of emission profiles of wood species growing in Portugal, in order to contribute with new data to source apportionment and information for an improved emission inventory development and to better understand the impact of these sources on human health, regional air quality and climate change.

2.2 Experimental

2.2.1 Wood selection

The most common softwood and hardwood in Portugal are, respectively, pine and eucalypts. This abundance in supply results in lower prices for these two wood types, thus rendering them as the main source for wood combustion in domestic fireplaces. Nevertheless, other wood types were also tested in this study (Table 2.1), because their use is widespread in the central and southern regions of Portugal, as in the case of oak, or as in the case of the golden wattle, in coastal areas, where it proliferates as an infesting species.

The elemental composition, ash and moisture content of all tested fuels are presented in Table 2.2.

Table 2.1 Portuguese tree species selected for wood stove combustion tests.

Common name	Scientific name	Species class	Kha forest	% Cover	Number of burning tests
Eucalypt	*Eucalyptus globulus*	Hardwood	541	16.3	4
Maritime pine	*Pinus pinaster*	Softwood	911	27.3	4
Cork oak	*Quercus suber*	Hardwood	331	9.9	3
Golden wattle	*Acacia longifolia*	Hardwood	19	0.6	3

Table 2.2 Elemental composition, ash and moisture content of biofuels (%w/w).

	C	H	N	S	O	Ash	Moisture
Eucalyptus globulus	43.5	4.57	0.12	0.01	38.7	0.66	12.5
Pinus pinaster	44.6	4.54	0.11	0.01	36.5	0.32	13.9
Quercus suber	44.8	4.19	0.15	0.01	35.6	0.43	14.8
Acacia longifolia	46.1	5.30	0.15	0.02	40.8	0.73	7.0

2.2.2 Sampling details

The burning tests were carried out at the combustion facility of the Vienna University of Technology, on a moderately sophisticated “chimney type” log woodstove for manual operation with a nominal power output of 6 kW. Combustion air enters the burning chamber (28x25x25cm) through a grate in the bottom (primary air) and a slit in the back wall (secondary air). The wood was cut into logs of 15 – 30 cm in length. Fires were ignited with small pieces cut from the same wood being burned and some lighter fuel. Burn times ranged between 95 and 139 minutes. Between 5.9 and 6.2 kg of wood were burned per test. Particle sampling began immediately prior to ignition and was ceased when the wood finished burning. A dilution source sampler was used for collecting the particulate matter from the flue gas.

The hot exhaust emissions are diluted (1:10) and remain in the residence chamber long enough to allow organic vapours to form particulate matter upon cooling in the

atmosphere instead of condensing onto pre-existing particles in the source exhaust within the dilution sampler itself. This provides ambient conditions to simulate gas-particle partitioning as it occurs in the atmosphere, downstream of the emission source. After a size separation step on filters, the aerosol particles are sampled. The size separation step is performed with a commercial low volume sampling head (Digitel AG, Switzerland) working on a one-stage impactor principle with a separation efficiency of 50% for particles with 10 μm aerodynamic diameter at a flow of 2.3 m^3 h^{-1}. The following manifold allows 8 aluminium filter holders (Pall Life Sciences) to be connected. The eight filter holders are equipped with 6 quartz fibre filters (Tissuquartz, Pall Life Sciences) for organic and ion analysis and 2 mixed cellulose ester filters (GN-4 Metricel, Pall Life Sciences) for metal analysis. The sample flow through quartz fibre filters was set to 0.29 m^3 h^{-1} per filter and, therefore, was double as high as through cellulose filters, with a flow of 0.15 m^3 h^{-1} per filter. This was necessary because of the high pressure drop of cellulose filters and the resulting lower maximum loads. The flows through both sampling lines were regulated with mass flow controllers (MFCs) (Bronkhorst) after drying the sampling gas with activated silica to refer the sampled volume to dry conditions. High efficiency particulate air (HEPA) capsules were used to protect MFCs from contamination. Finally, sampled gas volumes were measured with terminal dry gas meters. A detailed description of the experimental setup and its operational conditions can be found elsewhere (Schmidl et al., 2010).

2.2.3 Analytical methods

Gravimetric analysis was performed with a microbalance (Sartorius M5P) after 48h equilibration in a room with controlled temperature and humidity. Quartz fibre filters used in this work were pre-baked at 600ºC for 6 hours. Filter weight before and after sampling was obtained as the average of three measurements, when observed variations were less than 5%. For analysis of carbon species, small discs with 9 mm diameter were punched out of the quartz tissue filters with steel punches.

The carbonaceous content (EC/OC) of particulate matter in quartz fibre filters was analysed by a thermal-optical transmission technique (Alves et al., 2010a). The determination of levoglucosan, other sugars and polyols was performed by high-performance liquid chromatography (HPLC) with an electrochemical detector (Dionex

ED40, pulsed amperometry with gold working electrode) (Caseiro et al., 2007). The analytical procedure for the determination of cellulose in PM_{10} included an enzymatic conversion of total cellulose to D-glucose followed by its photometric detection (Sánchez-Ochoa et al., 2007). HULIS were pre-concentrated and cleaned-up by solid phase extraction with a size exclusion solid phase (ISOLUTE C18), which was followed by a further clean-up step using an anion exchange column (ISOLUE SAX) in a flow-injection system; the organic material eluting was quantified by on-line total organic carbon (TOC) determination (Limbeck et al., 2005). For the determination of soluble inorganic ions, small parts of the filters were extracted with ultra pure Milli-Q water. Dionex AS14 and CS12 chromatographic columns with Dionex AG14 and CG12 guard columns coupled to Dionex AMMS II and Dionex CMMS III suppressors, respectively for anions and cations, have been used. Cellulose acetate filters were used for metal analyses by inductively coupled plasma optical emission spectrometry (ICP-OES) and X-ray fluorescence spectroscopy (XRF) (Schmidl et al., 2008a). Radionuclides were measured by α-spectrometry after application of a sequential extraction and purification technique (Carvalho et al., 2007; Oliveira et al., 2006).

One quartz fibre filter from each burning test was extracted with dichloromethane (Fisher Scientific) and the total organic extract was separated into five different organic fractions by flash chromatography with silica gel and various solvents of increasing polarity. After each elution, the different fractions were vacuum concentrated and evaporated by ultra pure nitrogen stream. The detailed description of the methodology for the extraction of organic compounds can be found in Alves et al. (2010b). The fractionated extracts were analysed by gas chromatography–mass spectrometry (GC–MS). Before injection, the compounds with hydroxylic and carboxylic groups were converted into the corresponding trimethylsilyl derivatives by addition of N, O-bis(trimethylsilyl)triflouroacetamide (BSTFA): trimethylchlorosilane (TMCS) 99:1 (Supelco). Calibration for GC–MS analysis was based on a total of about 110 standards in different concentration levels with relative response factors determined individually for the majority of compounds. For those with no authentic standards available, relative response factors were calculated as an average from the overall homologous series or from compounds of similar chemical structure and retention time. Standards and samples were both co-injected with two internal standards: tetracosane-D_{50} (Sigma-Aldrich) and 1-

chlorohexadecane (Merck). The EPA 8270 semivolatile internal standard mix (Supelco), with six deuterated compounds (acenaphthene-d_{10}, chrysene-d_{12}, 1,4-dichlorobenzene-d_4, naphthalene-d_8, perylene-d_{12}, phenanthrene-d_{10}) has been used for determination of PAHs. Compound identification was based on comparison of resulting spectra with mass spectra library (Wiley 275), co-injection with authentic standards and analysis of fragmentation patterns.

2.3 Results and Discussion

2.3.1 Particulate emissions and carbonaceous content

Particulate matter emission factors from all wood combustion tests are presented in Figure 2.1. Emission factors ranged between 1.12±0.25 and 2.89±0.90 g per kg of wood burned (dry basis). Pine and golden wattle generate the lowest particle emissions, while the highest levels were produced by oak wood, followed by eucalypts. Fine et al. (2004b) obtained $PM_{2.5}$ emission factors for the combustion of American tree species in distinct residential appliances ranging from 0.88±0.16 g kg^{-1} to 3.4±0.5 g kg^{-1} (as fired). In particular, fine particle emissions for white oak and loblolly pine were 3.4±0.5 g kg^{-1} and 2.0±0.3 g kg^{-1} (as fired), respectively. PM_{10} emission factors for the combustion of *Acacia nilotica* in Indian traditional and improved stoves were 0.8-1.8 g kg^{-1} (dry basis) (Venkataraman and Rao, 2001). As stated in the literature, particle emission factors from residential biomass combustion may show wide variation due to the type of biomass burned, the characteristics of combustion facility, dilution techniques used and other differences observed in burning and sampling procedures (Fine et al., 2004b; Kowalczk et al., 1981; Lipsky and Robinson, 2006). According to Wardoyo et al. (2006), another important factor is the burning rate, with the highest particle emissions for slow burning conditions.

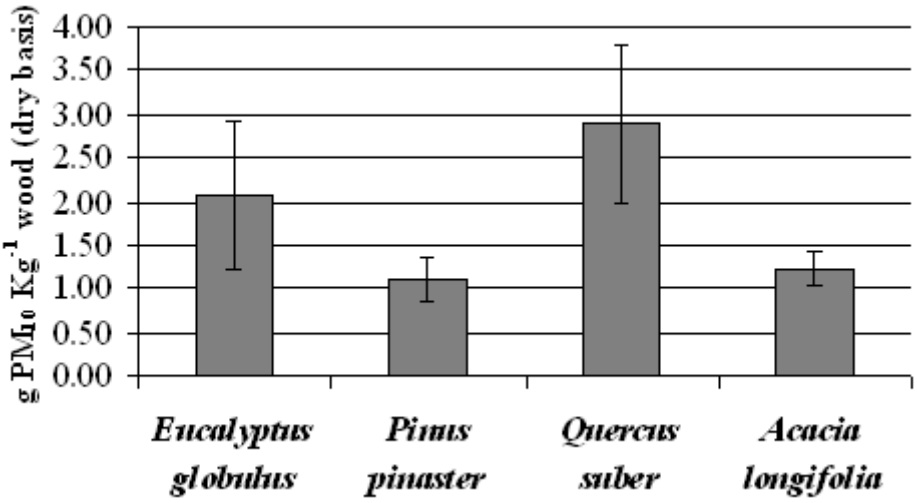

Figure 2.1 PM_{10} emission factors.

Organic and elemental carbon represented 43.9 to 63.2% (w/w) of the particulate mass emitted during the combustion process (Table 2.3). Burning pine, the only softwood among all species studied, generated the highest EC emissions (37.1% of PM_{10} mass), while oak smoke presented the lowest EC content (11.3% of PM_{10}). The OC content of PM_{10} ranged between 19.7% (golden wattle) and 42.8% (oak). The total carbon content of particle emissions from the combustion of Portuguese woods is comparable to those determined by Schmidl et al. (2008a).

Table 2.3 Carbonaceous components in wood smoke (%w/w PM_{10}).

	Wood Type	**TC**	**EC**	**OC**	**OC/EC**
E. globulus	Hardwood	45.2 ± 4.2	13.4 ± 8.3	31.8 ± 4.6	3.1
P. pinaster	Softwood	63.2 ± 5.9	37.1 ± 12.2	26.1 ± 10.3	0.9
Q. suber	Hardwood	54.1± 3.2	11.3 ± 4.5	42.8 ± 2.0	4.4
A. longifolia	Hardwood	43.9 ± 3.6	24.3 ± 9.7	19.7 ± 7.0	1.0
Alpine wood species (1)		64 - 74	10 - 21	49 - 56	2.6 - 5.7
American wood species (2)	Hardwood		3 - 23	51 - 59	2.6 - 17.3
American wood species (2)	Softwood		8 - 22	44 - 78	3.0 - 10.2

TC – Total Carbon = EC + OC; (1) Schimdl et al. (2008a); (2) Fine et al. (2004b).

The PM_{10} emitted from the Alpine hardwood (beech and oak) combustion consisted of around 20% and 50% of EC and OC, respectively. While the OC content of particle

emissions from burning Alpine softwoods is similar to that in hardwood smoke (≈50% of PM_{10}), the EC presented variable contributions (21% for spruce and 10% for larch). The $PM_{2.5}$ EC content from the stove combustion of prevalent USA hard- and softwoods were in the ranges 2-23% and 8-22%, respectively, whereas the OC mass fractions represented 51-54% (hardwood) and 44-78% (softwood) (Fine et al., 2004b). In addition to differences in biofuel types, the high EC fraction in aerosols emitted from wood burning in the tiled stove and in the chimney type log woodstove in comparison with values reported in the literature may be explained by the improved combustion efficiency in its combustion chamber. Higher combustion temperatures and stronger flaming conditions probably lead to the formation of more soot particles, enhancing the EC emissions (Chen et al., 2007). Differences between the results of this study and those of the literature may also arise from the use of distinct measurement techniques for EC and OC (Reisinger et al., 2008). The lower levels of OC in this study may be due, at least in part, to the fact that a portion of semi-volatile organic compounds had not condensed as a result of the slightly higher temperature in the dilution tunnel in comparison with the ambient atmosphere.

The ratio of OC/EC can be helpful in distinguishing carbonaceous sources. Lower ratios are characteristic of emissions from fossil fuel, while higher ratios are generally typical of biomass burning. Values ranging from 2.6 and 5.7 were reported for residential wood burning of Austrian biofuels (Schmidl et al., 2008a). McDonald et al. (2000) obtained an OC/EC ratio of 3.9 for softwood and 7.9 for hardwood in a woodstove. In this study, the highest OC/EC ratio was achieved for oak. At the opposite extreme, the lowest OC/EC values were obtained for pine emissions.

2.3.2 Inorganic speciation

Extractable ions, normally, are not major components of wood smoke, but, in this study, one of the wood species had a different behaviour. The golden wattle smoke presented a much higher ionic content, particularly due to Cl^-, Na^+ and K^+, than the emissions from the burning of the other wood types (Figure 2.2). This high ionic content may be related to the characteristics of the ecosystem where the trees have grown. The golden wattle wood came from coastal dunes permanently subjected to saltwater spray from the Atlantic Ocean and, from time to time, to tidal flooding. *Acacia* species have been described as one of the salt-tolerant non-halophyte groups with the ability to adjust

osmotically by utilising salts for maintaining turgor and thereby growth at high salinities (Ashraf et al., 2006).

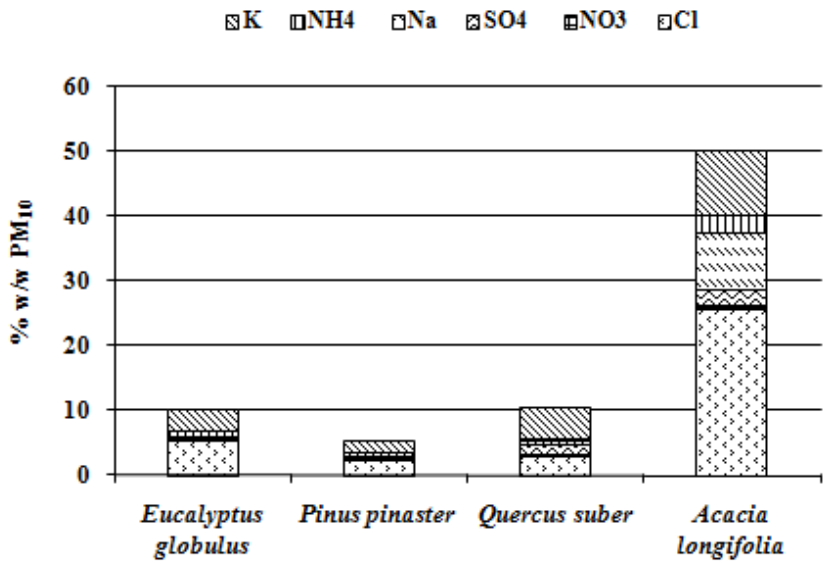

Figure 2.2 Mass concentration of water soluble ions in wood smoke (%w/w PM_{10}).

Potassium, often used as a wood smoke marker, shows some variability among different biofuels. Particle emissions from hardwood species exhibit higher K^+ contents than from softwoods. In accordance with these results, Fine et al. (2004b) reported K^+ mass concentrations in $PM_{2.5}$ of 1.014-2.740% and 0.458-1.171% for USA hard- and softwoods, respectively. The same researchers obtained chloride contents in $PM_{2.5}$ emissions of 0.278-0.839% for hardwood and 0.184-0.199% for softwood. Schmidl et al. (2008b) determined that soluble potassium represented 0.073 to 0.413% of the PM_{10} mass emitted from Woodstove combustion of common woods growing in mid-European Alpine regions, while the chloride and sodium contents were, respectively, 0.047-0.196% and 0.0092-0.038%. The concentration of most metals in smoke samples is low and differs greatly from those of other sources, such as vehicles (Lough et al., 2005). Since trees absorb these elements from water and soil, and considering that the availability of trace metals in soils can vary from region to region, then a lack of correlation among wood burning emission profiles in the literature is likely to exist. In this study, the highest metal content in PM_{10} was observed for golden wattle smoke. In general, the dominant metal elements were Ca, Co, Si and Fe (Figure 2.3).

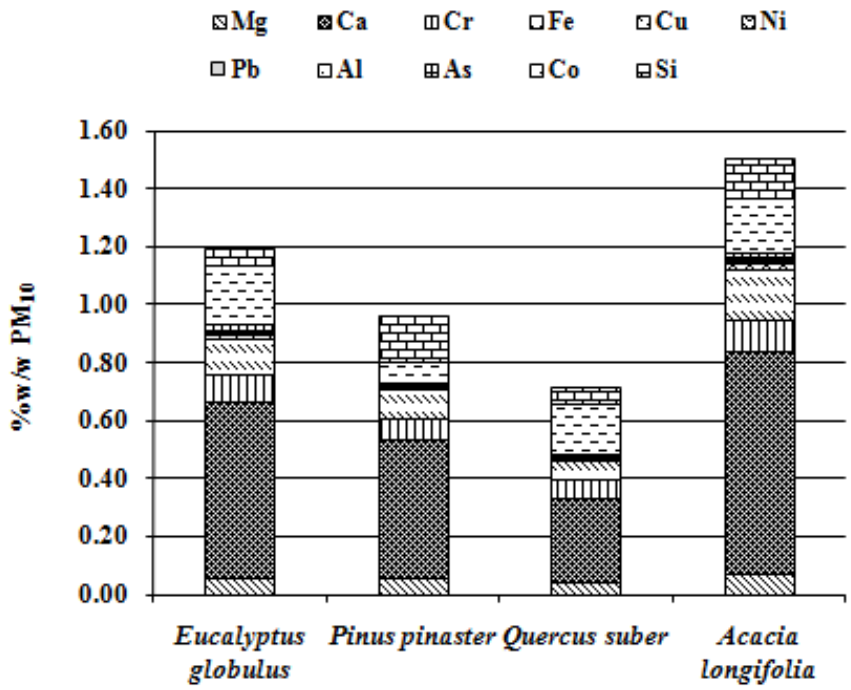

Figure 2.3 Mass concentration of metals in wood smoke (%w/w PM_{10}).

Analysis of the α-emitting products of the ^{238}U decay chain revealed that the ^{226}Ra was the naturally occurring radionuclide more enriched in PM_{10} (Table 2.4). The principal mechanism of incorporation into wood involves root uptake from soil and water. Typical concentrations in soils worldwide are 16-110 Bq kg^{-1} and 17-60 Bq kg^{-1} for ^{238}U and ^{226}Ra, respectively (Yaprak and Aslani, 2010). The concentrated radionuclides in the vegetation would be emitted to the atmosphere during burning, which could lead to serious environmental damage. Some of these radionuclides (e.g. ^{232}Th) are classified as carcinogens (Ishikawa et al., 2001; Prueitt et al., 2009).

Table 2.4 Radionuclides in wood smoke (Bq kg^{-1} PM_{10}).

	^{238}U	^{235}U	^{234}U	^{230}Th	^{226}Ra	^{232}Th
E. globulus	64.6 ± 5.2	2.8 ± 1.2	88.0 ± 6.6	40.4 ± 3.8	318 ± 65	34.7 ± 3.4
P. pinaster	<7.9	<6.4	2.4 ± 0.3	38.2 ± 3.9	98.3 ± 49.5	<12.4
Q. suber	10.0 ± 1.2	3.2 ± 1.1	11.8 ± 1.5	13.5 ± 2.6	12.4 ± 4.5	<17.3
A. longifolia	11.0 ± 1.4	3.4 ± 1.2	35.7 ± 4.2	68.3 ± 8.0	503 ± 165	<29

2.3.3 Organic speciation

The major organic components of smoke particles from biomass burning are monosaccharide derivatives from the breakdown of cellulose and hemicelluloses, such as levoglucosan, mannosan and galactosan (Simoneit et al., 1999) (Table 2.5). These anhydrosugars were found in high concentrations (0.2-17% w/w) for all wood types studied, except for golden wattle (0.07-1.9% w/w). As expected, levoglucosan, a specific marker for wood combustion in ambient PM samples (Jordan et al., 2006; Simoneit et al., 1999), was the most abundant organic compound. Average mass concentrations in PM_{10} ranged from 1.9% for golden wattle to 14.7% for eucalypts wood smoke, which is in general agreement with levoglucosan contents of 0.8-31.8% found for American woods (Fine et al., 2001, 2002, 2004a,b) and 4.1-15.1% obtained for Alpine tree species (Schmidl et al., 2008a). Mannosan was the second most abundant anhydrosugar product from the hemicellulose pyrolysis. Substantial differences in the concentrations between conifers (softwood) and deciduous (hardwood) trees were observed. Mass concentration values for deciduous trees range between 0.17% and 0.43%. On the other hand, the mannosan content in conifer tree smoke represented, on average, 1.3% of PM_{10}. Biomass smoke from conifers contains at least three times higher concentrations of mannosan than smoke from deciduous trees. Concluding, mannosan is a useful compound to distinguish between soft- and hardwood combustion, in agreement with what has been reported by Schmidl et al. (2008a). Considering the levoglucosan-to-mannosan ratio, the difference between hard- and softwood types becomes even more marked. The ratio was in the range 10.4–34.9 for hardwoods, while a value of 3.0 was encountered for softwood. Fine et al. (2004a) reported ratios around 19-26 and 5.4 for hardwood and softwood tree species, respectively. Schmidl et al. (2008a) obtained levo/man ratios of 3.6 and 14.8, respectively, for soft- and hardwoods. Galactosan was the third most abundant anhydrosugar in the wood smoke samples. Average PM_{10} mass concentrations of galactosan found in this study were 0.24% (pine), 0.22% (eucalypts), 0.18% (oak) and 0.07% (golden wattle). In smoke from Alpine trees species, galactosan mass concentrations were scattered over a wide range, from 0.2% to 4.5% (Schmidl et al., 2008a).

The most frequently occurring biopolymer in terrestrial environments is cellulose, because it is the basic structural material of many plants. Contrary to what one would expect, only small amounts of unburnt cellulose was found in wood smoke (Table 2.5).

Average mass concentrations ranged from 0.05% (oak) to 0.13% (eucalypts and pine). The average mass concentrations in the smoke from Alpine tree species was around 0.08% (Schmidl et al., 2008a).

Table 2.5 Anhydrosugars, cellulose and HULIS in wood smoke (%w/w PM_{10}).

	Eucalyptus globulus	***Pinus pinaster***	***Quercus suber***	***Acacia longifolia***
Levoglucosan	14.7 ± 4.4	3.8 ± 2.3	6.8 ± 0.97	1.9 ± 1.5
Mannosan	0.43 ± 0.14	1.3 ± 0.81	0.27 ± 0.04	0.17 ± 0.10
Galactosan	0.22 ± 0.08	0.24 ± 0.18	0.18 ± 0.02	0.07 ± 0.06
Levo/Man	34.9 ± 1.9	3.0 ± 0.59	24.8 ± 2.6	10.4 ± 4.0
Cellulose	0.13 ± 0.03	0.13 ± 0.11	0.05 ± 0.01	0.08 ± 0.01
HULIS	2.4 ± 0.62	3.0 ± 0.81	1.5 ± 0.43	1.7 ± 0.96

A class of organic molecules extracted from atmospheric aerosol particles and isolated from fog and cloud water has been termed HULIS due to a certain resemblance to terrestrial and aquatic humic and fulvic acids (Graber et al., 2006). The origin and formation pathways of such material are still under investigation. Results from recent studies show that these substances arise as secondary aerosol products from atmospheric processes with volatile organic compounds as precursors (Iinuma et al., 2007; Reinnig et al., 2008; Surratt et al., 2007, 2008). Nevertheless, Schmidl et al. (2008a) found HULIS in emissions from Alpine wood combustion, representing PM_{10} mass concentrations ranging from 0.57% to 5.8%. HULIS was also detected in very high amounts in leaf burning samples, contributing to 18.5-21.2% of the PM_{10} mass emissions (Schmidl et al., 2008b). In leaf burning samples the concentration was ten times higher than in wood combustion samples. Thus, it may be concluded that, besides the secondary formation path, HULIS can also be emitted as primary particles. In this study, average PM_{10} mass concentrations ranged from 1.5% (oak) to 3.0% (pine) (Table 2.5), well within the values reported for Alpine tree species.

Around 180 organic compounds have been identified. The concentrations of all these constituents can be found in appendix (Table A1), as supplementary material. These compounds can be volatilised molecules of the original naturally occurring components in the wood that condense again into the particle phase or, alternatively, chemical products of pyrolysis during combustion.

Aliphatic compounds comprised the *n*-alkane homologous series from C_{14} to C_{34} and *n*-alkenes ranging from C_{14} to $C_{29.}$ In accordance to what has been observed in smoke from domestic biomass burning in other studies (Rogge et al., 1998; Schmidl et al., 2008b), the *n*-alkane homologous series did not reveal any clear preference for molecules with an odd or even number of carbon atoms. The smoke emitted from eucalypts, pine and golden wattle contained approximately the same amount of *n*-alkanes, about 17 mg g^{-1}OC, while the content in oak emissions was 1.2 mg g^{-1}OC. In the case of *n*-alkenes, smoke from eucalypts and oak exhibited equivalent amounts, about 1.6 mg g^{-1}OC, whereas pine and golden wattle emissions contributed to 8.5 and 23.5 mg g^{-1}OC, respectively.

Twenty one PAHs and eight oxy-PAHs were identified in the smoke samples. The PAH emissions from pine combustion are significantly higher than those for the other wood types. Retene was the dominant aromatic hydrocarbon found in the softwood smoke (*Pinus pinaster* - 14.3 mg g^{-1}OC), whilst it was present at very small levels in the hardwood combustion emissions. Retene is the fully aromatised thermal alteration product of the resin acids present in conifer woods (Fine et al., 2001). The very high proportion of retene in softwood smoke was also verified by Fine et al. (2004b) in $PM_{2.5}$ emissions from the woodstove combustion of USA prevalent trees. In the American wood burning tests, retene represented 0.008–0.018 and 1.987–3.893 mg g^{-1}OC in hardwood and softwood smoke, respectively. Besides retene, fluoranthene and pyrene were the most prevalent PAHs found in both hardwood and softwood smoke. The dominant oxy-PAHs in all wood smokes were 9-fluorenone, 9H-xanthen-9-one and 9,10-anthracenedione.

Methoxyphenols have been identified as prominent lignin thermal degradation products and as semi-volatile components of smoke particles (Kjällstrand and Petersson, 2001). Softwood smoke contains 4-hydroxy-3-methoxyphenyl (guaiacyl or vanillyl) compounds, whereas hardwood burning contributes mainly to the formation of 4-hydroxy-3,5-dimethoxyphenyl (syringyl) compounds because of a different lignin structure. The predominant methoxyphenols found in the smoke were the vanillic and syringic acids. While vanillic acid was emitted at 15 mg g^{-1}OC in pine smoke, its content in samples from hardwood burning ranged from 4.93 to 11.5 mg g^{-1}OC. As expected, syringic acid was emitted at much higher levels in hardwood (26.3-35.4 mg g^{-1}OC) than in softwood smoke (1.75 mg g^{-1}OC).

β-Sitosterol was the most prevalent phytosterol emitted. Its high normalised-OC concentrations in eucalypts and oak emissions deserve consideration, suggesting the use of *β*-sitosterol as a potential tracer for these wood species. In general, its OC mass fraction exceeded the range (1.09–5.96 mg g^{-1}OC) reported for USA woods (Fine et al., 2004a). However, it cannot be regarded as a candidate to separate hardwood combustion emissions from softwood combustion emissions in source apportionment studies. Stigmasterol was only present in the smoke of hardwood species. This result is in accordance with the study by Fine et al. (2004b). Thus, stigmasterol may be pointed out as a potential tracer for smoke from deciduous trees.

Alkanoic acids ranging from C_8 to carbon number C_{24} were found in the smoke of the woods tested, exhibiting an even carbon number preference. All four wood smokes contained high levels of hexadecanoic acid as found in previous wood smoke studies (Fine et al., 2001, 2004b; Schmidl et al., 2008b). Docosanoic and tetracosanoic acids are also dominant compounds, especially in golden wattle and pine smoke. The only alkenoic acid found in all types of wood smokes was 9,12-octadecadienoic acid (linoleic acid), although at somewhat different levels. Alkanedioic acids and alkylated alkanoic acids were also detected to varying degrees in the emissions from the combustion of the four wood types. Particularly, heptanedioic acid (pimelic acid) was present at appreciable amounts, ranging from 3.31 to 8.04 mg g^{-1}OC. Resin acids such as isopimaric acid, dehydroabietic and pimaric acids were detected as significant components of softwood emissions but were found in trace quantities in the emissions from hardwoods. A significant fraction of acids, not possible to characterise individually, contributed to 144–649 mg g^{-1}OC.

A series of *n*-alkanols ranging from C_7 to C_{30} were present in the PM_{10} smoke samples. The homolog C_{18} was the dominant *n*-alkanol, even though its levels differed with wood type, standing out as a potential tracer for eucalypts smoke. The relatively high variety of *n*-alkanol homologs found in this study contrast with the rareness reported by Fine et al. (2001, 2004b), who have only found *n*-octadecanol, *n*-nonadecanol and *n*-eicosanol in the wood smoke samples. Unidentified alcohols may represent up to 220 mg g^{-1}OC.

It should be noted that the organic compounds mentioned as potential tracers (e.g. retene, methoxyphenols, phytosterols, resin acids and anhydrosugars) for hard- or softwood smoke have not been found in the tailpipe emissions from gasoline and diesel

powered vehicles (e.g. Pakbin et al., 2009; Schauer et al., 2002). Also, they have not been pointed out as tracers for other typical emission sources to ambient air, such as meat cooking, and plastic burning (Alves, 2008; and references therein). Thus, it is likely that these constituents can be used in source apportionment studies to estimate the contribution of biomass burning.

2.3.4 Mass balance

Taking into account the gravimetric data and all identified aerosol species, it is possible to reconstruct the PM_{10} mass emissions and to infer the organic matter-to-organic carbon (OM/OC) factor. This factor is used to compute the total organic mass concentration, accounting for associated O, H, N, and other elements, from the measured C mass concentrations attributed to OC. The equation used was as follows:

$$PM_{10} = \Sigma \text{ ionic species} + \Sigma \text{ metals} + EC + OC \times f \qquad (1)$$

where f represents the OM/OC ratio. Based on these calculations, average ratios of 2.4 (eucalypt and pine), 1.8 (cork oak) and 1.2 (golden wattle) were obtained. However, these values should be taken as upper limits due to the likely contribution of unmeasured species, which were not accounted for in the mass balance. After applying OM/OC ratios between 1.2 to 1.4 to the OC mass concentrations in $PM_{2.5}$ smoke from residential wood burning, Fine et al. (2001) observed that more than 100% of the gravimetric mass of the samples was assigned to measured chemical species. According to the researchers, the resulting mass overbalances were most likely caused by organic vapour adsorption onto the quartz fibre filters. In a review of biomass burning emissions focused on forest fires, Reid et al. (2005) reported OM/OC factors of 1.4-1.8. Nevertheless, based on the quantification of functional group composition of urban residential outdoor aerosols, Reff et al. (2007) obtained average OM/OC ratios ranging from 1.7 to 2.6, suggesting a higher polarity or degree of oxygenation of particles.

2.4 Conclusions

A gap is present in the characterisation of emissions from domestic burning of wood species with greater significance in Portugal. This research focused on the demand for new data to source apportionment, and on the extension and improvement of the existing inventories of wood burning emissions. Among the four wood species studied, pine (the only softwood in this study) generated the lowest particle emissions, while the highest levels were produced by oak, followed by eucalypts. On the other hand, pine produced the highest EC emissions, while oak smoke presented the lowest EC content in PM_{10}. Particle emission from golden wattle exhibited the lowest OC content and oak the highest. Golden wattle smoke presented a much higher ionic, particularly due to Cl^-, Na^+ and K^+, and metal contents than those in emissions from the burning of the other biofuels. In general, the dominant metal elements in smoke particles were Ca, Co, Si and Fe. Analysis of the α-emitting products of the ^{238}U decay chain revealed that the ^{226}Ra was the naturally occurring radionuclides more enriched in $PM_{10.}$ Contrary to what one would expect, unburnt cellulose was found in small amounts in wood smoke. HULIS presented average PM_{10} mass concentrations, lying within the values reported for Alpine tree species. The major organic components in particles from biomass burning were monosaccharide derivatives, in particular levoglucosan, acids and aliphatic compounds. Mannosan, a stereoisomer of levoglucosan, presented a substantial difference in concentrations between conifers (three times higher) and deciduous trees. Considering the levoglucosan/mannosan ratio, the difference between hard- and softwood types was even more discernible. Some of the identified organic compounds can be used as tracers of biomass burning and to distinguish between soft- or hardwood. Retene was the dominant aromatic hydrocarbon found in the softwood smoke, whilst it was present at very small levels in the hardwood combustion emissions. Guaiacyl and synapyl compounds were identified in softwood smoke, whereas hardwood burning contributed mainly to the formation of syringyl compounds, such as syringic acid. Stigmasterol was only present in the smoke of hardwood species; thus, this compound may be pointed out as a potential tracer for smoke from deciduous trees.

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CHAPTER 3

Chapter 3. Organic compounds in $PM_{2.5}$ emitted from fireplace and woodstove combustion of typical Portuguese wood species

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Abstract

The aim of this study is the further characterisation of $PM_{2.5}$ emissions from the residential wood combustion of common woods grown in Portugal. This new research extends to eight the number of biomass fuels studied and tries to understand the differences that the burning appliance (fireplace versus woodstove) and the combustion temperature (cold and hot start) have on emissions. *Pinus pinaster* (Maritime pine), *Eucalyptus globulus* (eucalypt), *Quercus suber* (cork oak), *Acacia longifolia* (Golden wattle), *Quercus faginea* (Portuguese oak), *Olea europea* (Olive), *Quercus ilex rotundifolia* (Holm oak) and briquettes produced from forest biomass waste were used in the combustion tests. Determinations included fine particle emission factors, carbonaceous content (OC and EC) by a thermaloptical transmission technique and detailed identification and quantification of organic compounds by gas chromatography–mass spectrometry. Fine particle emission factors from the woodstove were lower than those from the fireplace. For both combustion appliances, the OC/EC ratio was higher in "cold start" tests (1.56±0.95 for woodstove and 2.03±1.34 for fireplace). These "cold start" OC/EC values were, respectively, for the woodstove and the fireplace, 51% and 69% higher than those obtained in "hot start" experiments. The chromatographically resolved organics included *n*-alkanes, *n*-alkenes, PAHs, *n*-alkanals, ketones, *n*-alkanols, terpenoids, triterpenoids, phenolic compounds,

phytosterols, alcohols, *n*-alkanoic acids, *n*-di-acids, unsaturated acids and alkyl esters of acids. The smoke emission rate and composition varied widely depending on fuel type, burning appliance and combustion temperature.

Keywords: biomass burning, fireplace, woodstove, $PM_{2.5}$, GC-MS, organic tracers.

3.1 Introduction

Residential wood log combustion is considered to be a major emission source of local and regional air pollution, especially for particulate matter and hydrocarbons, such as polycyclic aromatics (Fine et al., 2004b; Rogge et al., 1998; Schimdl et al., 2008a). The flue gases from residential biomass combustion are dominated by submicron particles (<1 μm) by number and often also by mass, and there is an increasing interest in their characteristics and implications to human health (Lighty et al., 2000). Besides the health-related implications, these aerosols have climate-forcing impacts, either contributing to, or balancing, the effects of greenhouse gases (Danny and Kaufmann, 2002). In Europe, emissions from biomass combustion are one of the major sources of atmospheric aerosol mass during winter (Gelencsér et al., 2007; Puxbaum et al., 2007). Modelling results showed that in Portugal 18% of PM_{10} could be related to this emission source, which may deeply impact the levels in the atmosphere (Borrego et al., 2010). Source apportionment of $PM_{2.5}$ aerosol applied to the ambient measurements in a coastal/rural area in Portugal showed that 52 – 69% of the organic carbon is assigned to residential wood burning for heating (Gelencsér et al., 2007). Responses to a national survey (unpublished data) indicated that, on average, 34% of the Portuguese population uses residential wood combustion for heating purposes, but this percentage can reach 62% in cold inland districts, such as Viseu. In Portugal and other Mediterranean countries, there is a lack of information concerning the characteristics of particulate emissions from biomass combustion systems. Emission inventories and source apportionment, studies (e.g. Caseiro et al., 2009; Kupiainen and Limonet, 2007; Yin et al., 2010) have been using default values obtained for United States (e.g. Fine et al., 2004a,b), mid-European Alpine region (Schmidl et al., 2008a), or Scandinavian (Hedberg et al., 2002; Johansson et al., 2004) biofuels, uncommon in Southern Europe. Because of the lack of biomass burning profiles for Southern Europe, positive matrix factorisation or principal components analysis (unknown sources) instead of chemical mass balance (known sources) have been used to apportion different inputs to the ambient aerosol (e.g. Callen et al., 2009). To overcome the lack of information, a series of source tests were made to evaluate the chemical composition of particulate matter (PM_{10}) emissions from the woodstove combustion of four prevalent Portuguese species of wood: *Pinus pinaster*, *Eucalyptus globulus*, *Quercus*

suber and *Acacia longifolia*. The burning tests were carried out at the combustion facility of the Vienna University of Technology, on a highly efficient "chimney type" log woodstove and the results were published by Gonçalves et al. (2010). The objectives of this new investigation are to extend to eight the number of biomass fuels studied and try to understand the effects of traditional Portuguese burning appliances (a brick open fireplace versus a cast iron woodstove) and combustion conditions on emissions. In addition to a larger number of wood species involved in the present study in comparison to that in Gonçalves et al. (2010), the two major differences between both investigations are related to the use of burning appliances with distinct characteristics ("chimney type" stove in Austria with high efficiency versus traditional Portuguese equipments with lower efficiency) and sampling of particulate matter with distinct aerodynamic diameters (PM_{10} for the Austrian stove, $PM_{2.5}$ for the Portuguese appliances).

Characterisation of the emissions for different types of appliances during different operation conditions (cold and hot start phases) makes it possible to identify when the major parts of the emissions occur and actions for emission reduction can then be achieved where the savings can be highest. On the other hand, by weighting the source test results in proportion to the availability of firewood from specific tree species, the quantities of wood burned in each region, type and number of household burning appliances, and prevailing combustion conditions in "ordinary" domestic operation, it will be possible to develop composite regional source profiles for Chemical Mass Balance receptor models, to account for particulate organic emissions at a country-scale and to quantify the regional differences in wood smoke composition.

3.2 Experimental work

3.2.1 Biomass fuel selection

According to the Portuguese Forest Inventory (2005), the top seven nationally predominant tree species are *Pinus pinaster* (Maritime pine), *Eucalyptus globulus* (Eucalypt), *Quercus suber* (Cork oak), *Acacia longifolia* (Golden wattle), *Quercus faginea* (Portuguese oak), *Olea europea* (olive) and *Quercus ilex rotundifolia* (Holm oak). The burning emissions of all these species were studied and results are presented here. In addition, biomass briquettes made of wastes from forest cleaning activities and/or wastes

from local wood processing industries, common in home heating nowadays, were also studied and evaluated. The elemental composition, ash and moisture content of all tested fuels are presented in Table 3.1.

Table 3.1 Elemental composition, ash and moisture content of biofuels (%w/w).

Biomass	**% Moisture content**	**Elemental composition (dry basis)**					**Ashes**
		C	**H**	**N**	**S**	**O (by difference)**	
Maritime pine	9.10	51.4	6.20	0.160	n/d	41.9	0.360
Eucalypt	11.3	48.6	6.20	0.160	n/d	44.3	0.750
Cork oak	12.2	51.6	6.03	0.180	n/d	40.8	1.41
Olive	15.5	53.6	7.68	0.180	n/d	36.6	1.94
Portuguese oak	14.1	50.3	7.32	0.190	n/d	41.8	0.380
Holm oak	8.70	50.6	7.14	0.180	n/d	39.7	2.32
Golden wattle	8.40	50.8	6.43	0.180	n/d	41.8	0.750
Briquettes	8.40	50.8	7.01	0.160	n/d	41.2	0.910

n/d – not determined because the concentration level was below detection level of 0.01%w/w.

3.2.2 Sampling details

The burning tests were carried out at the Department of Environment, University of Aveiro, combustion facility. The facility structure and operational conditions were described in detail by Fernandes (2009). Two types of residential biomass combustion appliances were selected for the source tests: i) a cast iron woodstove (Solzaima, model Sahara), operated manually in batch mode with handheld control of combustion air, and ii) a traditional Portuguese brick open fireplace operated manually in batch mode and with no control of combustion air. In order to evaluate the influence of the temperature and fuel ignition process on the combustion flue emission characteristics, two sets of experiments were performed for each appliance and wood fuel type: cold start and hot start. In the experiments with cold start, the combustion began with the appliance at ambient temperature. Thus, the "cold start" experiments represent the post-ignition combustion phase. The hot start experiments were initiated with the load of a batch of fuel to the combustion chamber already at a temperature of around 100ºC and with the presence of a small amount of burning char from a batch of fuel already burned previously. The continuous monitoring of temperatures was made with K-type thermocouples in the middle

point of each combustion chamber. The temperature in the combustion chamber of the fireplace, on average, was 128ºC±66ºC for "cold start" and 179ºC±63ºC for "hot start". The temperature in the combustion chamber of the woodstove, on average, was 248ºC±69ºC for "cold start" and 307ºC±67ºC for "hot start". It should be noted that Tiegs (1995) reported that the cold start-up PM emissions can be about half of the emissions from a full combustion cycle. Thus, emissions from different combustion phases should be accounted for in order to develop composite emission profiles for further application in source apportionment methodologies.

The wood was cut into logs of 30 – 40 cm in length. Before each burning test, a batch of dry wood was weighed in a balance. The weights ranged between 1.9 and 2.2 kg. The ignition of the wood was achieved using small pieces cut from the same wood being burned. Burn times ranged from 45 to 90 minutes. Particle sampling began immediately prior to ignition and was ceased at the end of combustion. Collection of particulate matter with aerodynamic diameters below 2.5 μm ($PM_{2.5}$) was performed in a dilution tunnel. Dilution sampling is used to characterise particle emissions from combustion because it simulates the rapid cooling and dilution that occurs as exhaust mixes with the atmosphere (Lipsky and Robinson, 2005). The dilution tunnel consisted of a cylindrical tube with 0.20 m internal diameter and 11 m length. The sampling of $PM_{2.5}$ was made at a dilution ratio of 25:1. $PM_{2.5}$ were collected using an Echo sampling head connected to a TECORA sampler (model 2.004.01, Italy) operating at a flow of 2.3 $m^3\ h^{-1}$, onto quartz fibre filters (47 mm diameter), located at 10 m downstream the dilution tunnel entering. The temperature in the particle sampling point in the dilution tunnel was in the range 25–35ºC.

After each combustion experiment, the $PM_{2.5}$ sampling head was cleaned to minimise contamination of the subsequent experiments. Background samples were collected to assess any contamination arising from the dilution air; negligible levels of particulate matter, organic carbon and elemental carbon were found. The conditions at the exit of the chimney of the woodstove or fireplace are different from those in the dilution tunnel. For this reason, the $PM_{2.5}$ concentrations at the exit of the chimney were obtained by correcting the concentrations measured at the dilution tunnel, considering the respective values of temperature, pressure and dilution ratio.

3.2.3 Analytical methods

Gravimetric analysis was performed with a microbalance (Sartorius M5P) after 24 h equilibration in a room with controlled temperature and humidity. Quartz fibre filters used in this work were pre-baked at 500ºC for 6 hours. Filter weight before and after sampling was obtained as the average of three measurements, when observed variations were less than 5%.

The elemental carbon (EC) and organic carbon (OC) of particulate matter in quartz fibre filters were analysed by a thermal–optical technique. The carbon analyser was a home-made thermo-optical system, based on the thermal desorption/oxidation of particulate carbon to CO_2, which is subsequently analysed by non-dispersive infrared spectrophotometry (Pio et al., 1993). Controlled heating in anoxic conditions was performed to separate OC into two fractions of increasing volatility. The first fraction corresponds to the volatilisation at T<200ºC of lower molecular weight organics (OC1). The second fraction is related to decomposition and oxidation of higher molecular weight species at temperatures ranging from 150 to 600ºC (OC2). The last fraction of OC is identified by transmittance and corresponds to pyrolysed organic carbon (PC) produced in the previous heating steps. Separation between OC and EC was achieved by initially heating the filter punches under an inert atmosphere to evaporate first the OC fraction. The remaining fraction is sequentially evaporated/burnt under a gas flow containing O_2. This last carbon fraction contains initial EC plus OC that has pyrolysed during heating under an inert atmosphere. The interference between PC and EC can be controlled by continuous evaluation of the blackening of filter using a laser beam and a photodetector measuring the filter light transmittance (Alves et al., 2011a).

Half of the area of each quartz fibre filter was consecutively extracted with dichloromethane and methanol (Fisher Scientific) and the total organic extract was separated into five different organic fractions by flash chromatography with silica gel and various solvents of increasing polarity. After elution, the different fractions were vacuum concentrated and evaporated by ultra pure nitrogen stream. The detailed description of the methodology for the extraction of organic compounds can be found in Alves et al. (2011a). The fractionated extracts were analysed by gas chromatography–mass spectrometry (GC model 6890, quadrupole MSD 5973 from Hewlett Packard and GC Trace Ultra, quadrupole DSQ II from Thermo Scientific). Before injection, the compounds with

hydroxylic and carboxylic groups were converted into the corresponding trimethylsilyl derivatives by addition of N, O-bis(trimethylsilyl)triflouroacetamide (BSTFA): trimethylchlorosilane (TMCS) 99:1 (Supelco). Calibration for GC–MS analysis was based on a total of about 110 standards in different concentration levels with relative response factors determined individually for the majority of compounds. For those with no authentic standards available, relative response factors were calculated as an average of the relative response factors from the overall homologous series or from compounds of similar chemical structure and retention time. Standards and samples were both co-injected with two internal standards: tetracosane-D_{50} (Sigma Aldrich) and 1-chlorohexadecane (Merck). The EPA 8270 Semivolatile Internal Standards Mix (Supelco), with six deuterated compounds (acenaphthene-d_{10}, chrysene-d_{12}, 1,4-dichlorobenzene-d_4, naphthalene-d_8, perylene-d_{12}, phenanthrene-d_{10}) was used for the determination of PAHs. Compound identification was based on comparison of resulting spectra with mass spectra libraries (Wiley 275 and NIST MS Search 2.0), co-injection with authentic standards and analysis of fragmentation patterns.

3.3 Results and Discussion

3.3.1 $PM_{2.5}$ emission factors and carbonaceous content

$PM_{2.5}$ emission factors and the carbonaceous content were calculated for the woodstove and fireplace with both cold and hot starts, as shown in Figures 3.1 and 3.2. The $PM_{2.5}$ emission factors were in the range from 5.62 to 25.8 g kg^{-1} (dry basis) (cold start) and from 1.66 to 16.0 g kg^{-1} (dry basis) (hot start) of fuel burned in the woodstove. The emission factors for fireplace were between 8.11 and 29.0 g kg^{-1} (dry basis) (cold start) and 0.84 to 21.7 g kg^{-1} of fuel burned (dry basis) (hot start). The emission factor of $PM_{2.5}$ was always higher during the combustion experiments in the fireplace than in the woodstove. In general, particulate matter emissions were higher during the experiments with cold start for both equipments (Figure 3.1).

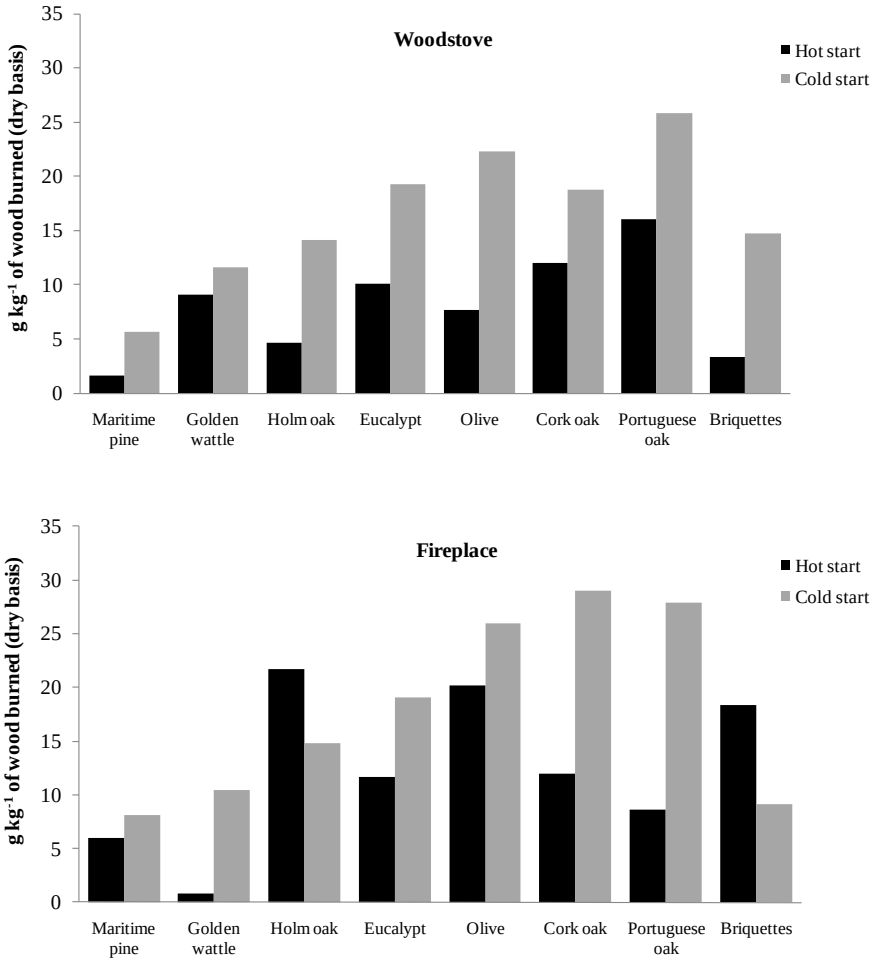

Figure 3.1 $PM_{2.5}$ emission factors (dry fuel basis).

This is related to the fact that under those conditions the temperature in the combustion chamber is lower. Lower temperatures results in a lower degree of conversion (oxidation) of the biomass (solid and pyrolysis products), thus originating a higher emission of unburned chemical compounds. The emissions from the combustion of maritime pine whether in the woodstove or in the fireplace were the lowest among all biomass fuels. Fine et al. (2001, 2002, 2004b) obtained $PM_{2.5}$ emission factors for the fireplace and woodstove combustion of American tree species lower than those observed in this study; the $PM_{2.5}$ emission factors were in the range 0.88 – 3.4 g kg^{-1} of wood burned (as fired) in a woodstove, and between 1.6 and 11.4 g kg^{-1} of wood burned (as fired) in the fireplace. As stated in the literature, particle emission factors from residential biomass combustion may show wide variation due to the type of fuel, the characteristics of

combustion facility, dilution techniques used, sampling procedures, burning rate and the moisture content of the fuel (Fine et al., 2004b; Kowalczk et al., 1981; Lipsky and Robinson, 2005; Wardoyo et al., 2006). Burning wood of poor quality (e.g. high moisture content), overloading the firebox or insufficient air supply, are examples of conditions that can lead to incomplete combustion, characterised by low temperature (Bølling et al., 2009). Lipsky and Robinson (2005) tested the effects of dilution on fine particle mass concluding that too little dilution can potentially overestimate the fine particle mass emissions, and too much dilution can underestimate them. At low levels of dilution semivolatile species largely occur in the particle phase, but increasing dilution reduces the concentration of semivolatile species, shifting this material to the gas phase in order to maintain phase equilibrium. It should be noted, however, that the dilution ratio used in our study is comparable to the majority of values reported in the literature for biomass burning experiments (Lipsky and Robinson, 2005). The $PM_{2.5}$ emission factors for the fireplace and the woodstove are in the range of values reported for identical household combustion appliances in Scandinavia (Bølling et al., 2009; and references therein). However, particle emissions from the woodstove are much higher than those obtained in the "chimney type" stove (Gonçalves et al., 2010) and in other modern combustion devices (Bølling et al., 2009). Thus, it seems that the major differences in emission factors are due to large variations in combustion appliance types.

Total carbon represented 38% w/w (hot start) to 52% w/w (cold start) and 21% w/w (cold start) to 55% w/w (hot start) of the particle mass emitted during the combustion processes in the woodstove and fireplace, respectively (can be deduced in Figure 3.2). Combustion of maritime pine, the only softwood among all species studied, in both combustion equipments generated the highest EC content in $PM_{2.5}$ (fireplace with hot start: 17% w/w; woodstove with hot start: 9.3% w/w), while briquette-derived smoke presented the lowest EC content (fireplace with cold start: 1.1% w/w; woodstove with cold start: 0.82% w/w). The OC content of $PM_{2.5}$ ranged between 30% w/w (briquettes - hot start) and 50% w/w (cork oak – cold start) for tests carried out in the woodstove. In the fireplace, the lowest OC content (cold start: 20% w/w) was observed during eucalypt combustion, while the smoke aerosols from the combustion of cork oak were the most OC-enriched (cold start: 48% w/w) (Figure 3.2). The carbon content of particle emissions from the

combustion of Portuguese woods was compared with that determined by Fine et al. (2001, 2002, 2004b) and by Gonçalves et al. (2010) in Table 3.2.

Table 3.2 Carbonaceous content in smoke particles (minimum and maximum values).

Carbonaceus content	**Woodstove (% w/w)**	**Fireplace (% w/w)**	
TC	38 (h.s.) - 52 (c.s.)	21(c.s.) - 55 (h.s.)	**This study**
EC	0.82 (c.s. - briquettes) – 9.3 (h.s. - maritime pine)	1.1 (c.s. - briquettes) – 17 (h.s. - maritime pine)	
OC	30 (h.s. - briquettes) - 50 (c.s. - cork oak)	20 (c.s. - eucalypt) - 48 (c.s. - cork oak)	
EC	3.3 - 22.8 (hardwood) 7.6 - 13.4 (softwood)	1.2 - 22.0 (hardwood) 5.4 - 31.3 (softwood)	Fine et al., 2001, 2002, 2004b
OC	51.2 - 59.4 (hardwood) 43.6 - 77.8 (softwood)	74.2 - 87.5 (hardwood) 73.4 - 102.3 (softwood)	
TC	43.9 - 63.2		Gonçalves et al., 2010
EC	11.3 (cork oak) - 37.1 (maritime pine)		
OC	19.7 (golden wattle) - 42.8 (cork oak)		

h.s. – hot start; c.s. – cold start.

This study - $PM_{2.5}$; Fine et al. - $PM_{2.5}$; Gonçalves et al. - PM_{10}

The OC values obtained by Fine et al. (2002) for the fireplace combustion of selected American wood species are about two times higher than those obtained in our study. It should be noted, however, that Fine et al. (2002) obtained, in several tests, OC/PM ratios higher than 100%. They explained the results by increased organic vapour adsorption onto the quartz fibre filters used for organics collection relative to the Teflon filters from which gravimetric mass measurements were taken. Since no reliable method exists to correct for this positive adsorption artefact, and considering the possibility of a negative artefact caused by desorption of particle phase compounds, no correction was made by the researchers to the OC data.

It should be noted that the carbonaceous content obtained from thermal-optical technique does not account for associated O, H, N, and other elements, from the measured C mass concentrations attributed to OC. To estimate the organic matter content in particulate matter, the OC measurements have to be multiplied by a factor ranging from 1.4

to 2 (Alves et al., 2011a; Gonçalves et al., 2010). Thus, up to 90% of the $PM_{2.5}$ in the wood smoke is constituted by organic matter. The inorganic composition of smoke particles from these residential biomass burning samples was discussed in detail by Alves et al. (2011b), who found that the water-soluble ions accounted for about 1 to 14% of the $PM_{2.5}$ mass, while trace elements represented 0.4 to 2.5%.

The OC/EC ratio of $PM_{2.5}$ in the woodstove ranged between 3.99 (briquettes – hot start) and 52.58 (briquettes – cold start). For the fireplace emissions, the OC/EC varied from 2.23 (maritime pine – hot start) to 35.49 (briquettes – cold start) (Figure 3.2). The OC/EC ratio can be helpful in distinguishing carbonaceous sources. Lower ratios are characteristic of fresh emissions from fossil fuel, while higher ratios are generally typical of biomass burning. High OC production in wood combustion emissions has been attributed to condensation of large hydrocarbons, enhanced isoprenoid emissions, acid-catalysed reactions and very rapid oxidation of low-volatility organic vapours (Grieshop et al., 2009; and references therein). Values ranging from 2.6 to 5.7 were reported for residential wood burning of Austrian biofuels (Schmidl et al., 2008a). McDonald et al. (2000) obtained an OC/EC ratio of 3.9 for softwood and 7.9 for hardwood in a woodstove. Gonçalves et al. (2010) reported ratios ranging from 0.9 for maritime pine PM_{10} emissions to 4.4 for the smoke of cork oak emitted from the combustion in a "chimney type" stove. Higher OC/EC ratios have been reported for low-temperature combustion in conventional fireplaces and stoves, confirming that particulate matter from these appliances are dominated by OC (Bølling et al., 2009), while higher EC mass fractions in smoke particles from the combustion of woody biomass in more efficient modern small scale units (modern log woodstoves with secondary air and automated air supply, and pellet stoves) contributed to lower OC/EC ratios, sometimes comparable to those from vehicular emissions. Ratios <1 have been determined at tunnel and roadside sites, where vehicle exhausts were the dominant sources of aerosols (Cheng et al., 2010). Monitoring campaigns in a busy roadway tunnel in central Lisbon showed OC/EC ratios between 0.3 and 0.4 (Pio et al., 2011).

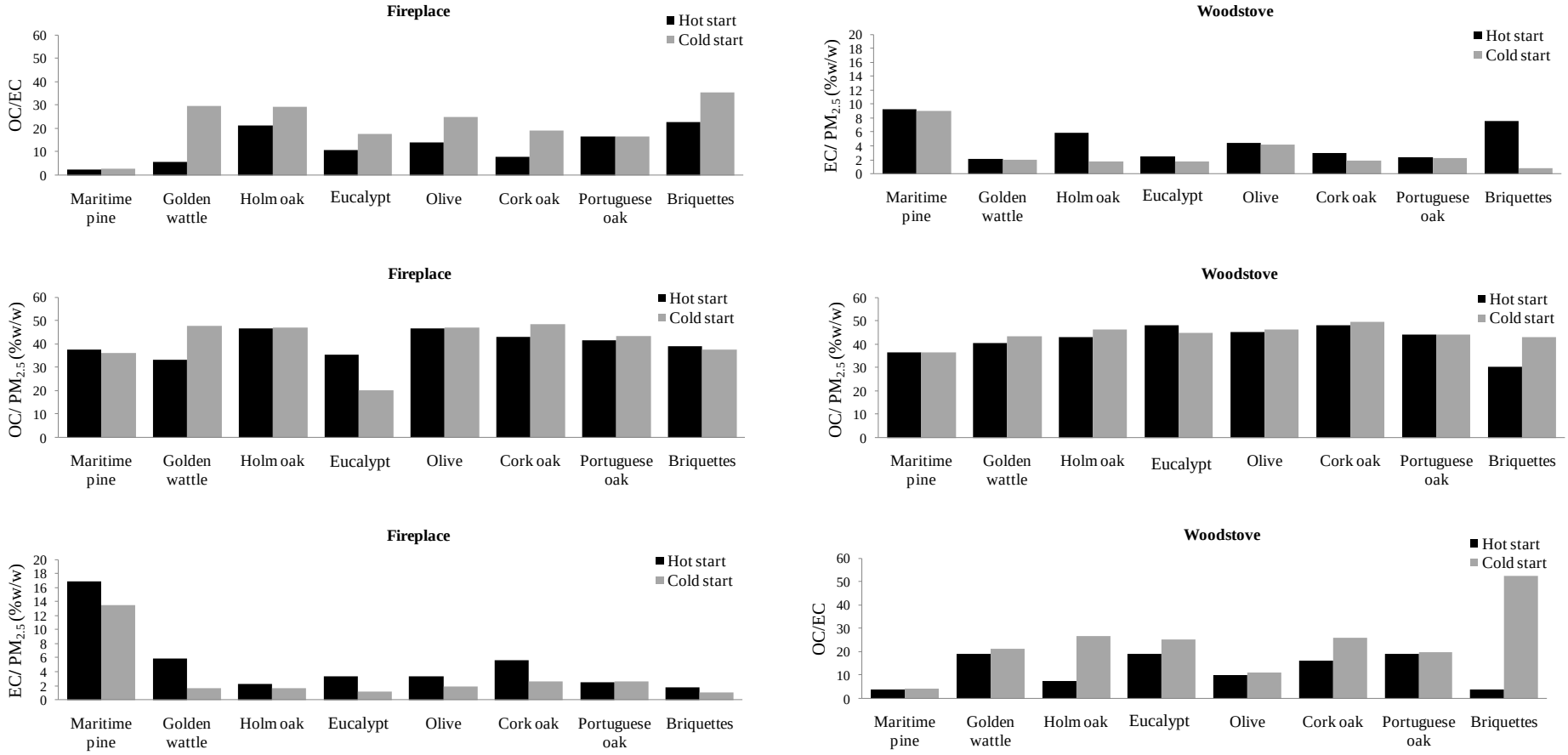

Figure 3.2 Carbonaceous components: elemental carbon (EC), organic carbon (OC) and OC/EC in $PM_{2.5}$.

3.3.2 Organic speciation

The organic compounds found in biomass burning emissions can have two distinct origins: may result, either from volatilisation of organic molecules originally present in the wood that recondense into particle phase, or from pyrolysis products of combustion reactions (Fine et al., 2001). Thus, some organic compounds may be directly released by a steam stripping/volatilisation effect, while others are pyrolysis derivatives from the thermal breakdown of cellulose, lignin and other biopolymers. Natural (unaltered) and thermally altered (pyrolysis) derivative compounds emitted by biomass burning can be utilised as specific indicators for identifying inputs from this specific source. In this study, more than one hundred eighty organic compounds were identified. The OC-normalised concentrations of all these constituents can be found in appendix (Table A2), as supplementary material. The database obtained is potentially useful to improve existing emission inventories. In addition, these results will supply important information on the variability in wood smoke tracer emission rates for those organic compounds that are presently used in receptor models.

3.3.2.1 Homologous compound series

Aliphatic compounds comprised the *n*-alkane homologous series from C_{14} to C_{34} and *n*-alkenes from C_{16} to $C_{28.}$ In accordance to what has been observed in other studies of domestic biomass burning smoke (Rogge et al., 1998; Schmidl et al., 2008b), the *n*-alkane homologous series did not show any clear preference for molecules with an odd or even number of carbon atoms. The homologues with the highest concentrations (C_{max}) were C_{14} and C_{23}. For alkenes, the C_{max} was at C_{22}. Alkenes are probably derived from the dehydration of *n*-alkanols (Simoneit et al., 2000). A similar distribution is observed for the *n*-alkanols and thus an origin from reduction of *n*-alkanoic acids or cracking of wax *n*-alkanes is less likely (Simoneit, 2002). Independently from the burning appliance, the highest alkane concentrations were observed in tests with cold start. Weisenberg et al. (2009) showed that the distribution patterns of *n*-alkanes in biomass burning samples (maize and rye straw) changed as a function of temperature. At higher combustion temperatures, *n*-alkanes seem to be less stable than other compounds (Schmidl et al., 2008b). During the charring process, the long-chain *n*-alkanes may suffer thermal

breakdown, causing short-chain homologues with a maximum at $<C_{20}$. Hence, the predominance of short-chain homologues, instead of C_{max} at C_{27}, C_{29} or C_{31} typical of vegetation waxes, was found to be a useful marker for incomplete burning of biomass (Eckmeier and Wiesenberg, 2009). The species whose smoke contained the highest amount of alkanes were golden wattle (fireplace with cold start) and maritime pine (woodstove with hot start) (Figure 3.3).

The alkenes were emitted aplenty by the woodstove with hot start and by fireplace with cold start. Golden wattle was the wood species whose smoke presented the highest *n*-alkenes content (Figure 3.4). The higher amount of aliphatic compounds in the smoke emitted from maritime pine and golden wattle and the lower content in cork oak emissions are consistent with previous measurements in a woodstove (Gonçalves et al., 2010).

The smoke samples revealed the presence of an incomplete homologous series of *n*-alkanols from C_{10} to C_{30}. Depending on the sample, various C_{max}, in the range from C_{18} to C_{28}, were found. The C_{22} homologue was the most representative. In general, the *n*-alkanols in the smoke from the combustion in the fireplace contributed to a higher fraction of OC (average = 2.02 mg g^{-1}) than that observed in emissions from the woodstove (average = 1.21 mg g^{-1}). Olive (fireplace with cold start) and eucalypt (fireplace with cold start) were the wood species with the highest *n*-alkanol content in $PM_{2.5}$ emissions, whilst the smallest amounts were detected in the Maritime pine smoke (woodstove with cold start and fireplace with cold start) (Figure 3.5).

A series of *n*-alkanoic acids were identified in the smoke of all samples, ranging from C_8 to C_{24}. These homologous series are ubiquitous in biomass burning smoke (Simoneit, 2002). These acids were generally emitted in large amount by both combustion equipments with hot start. All wood smokes contained high levels of both hexadecanoic and tetracosanoic acids, as found in previous biomass burning studies (Fine et al., 2001, 2004b; Gonçalves et al, 2010; Schmidl et al., 2008b; Simoneit, 2002).

The total OC-normalised concentrations of all *n*-alkanoic acids were in the range from 0.548 mg g^{-1}OC (cork oak – fireplace with cold start) to 39.9 mg g^{-1}OC (Portuguese oak – fireplace with hot start) (Figure 3.6). The only alkenoic acid found in all types of wood smokes was 9,12-octadecadienoic acid (linoleic acid), in a range between 0.11 mg g^{-1}OC (fireplace with hot start – olive) and 7.05 mg g^{-1}OC (woodstove with cold start – briquettes).

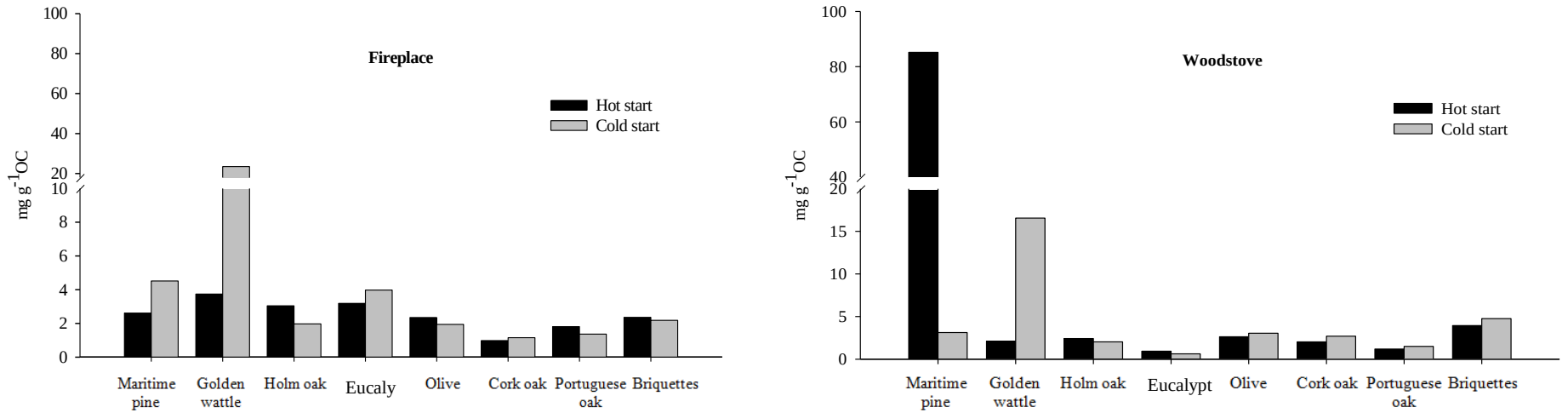

Figure 3.3 OC-normalised concentrations of Σ alkanes in the $PM_{2.5}$ from the various biomass fuels.

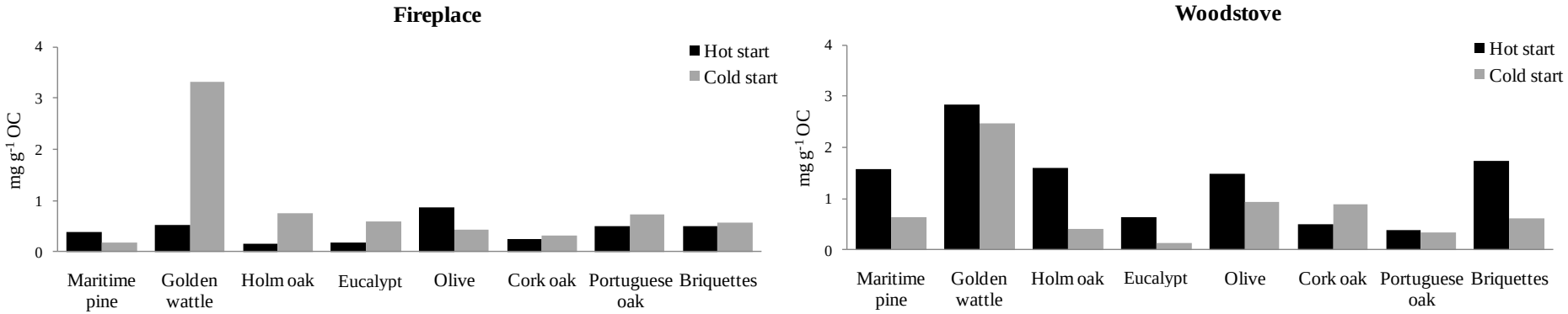

Figure 3.4 OC-normalised concentrations of Σ alkenes in the $PM_{2.5}$ from the various biomass fuels.

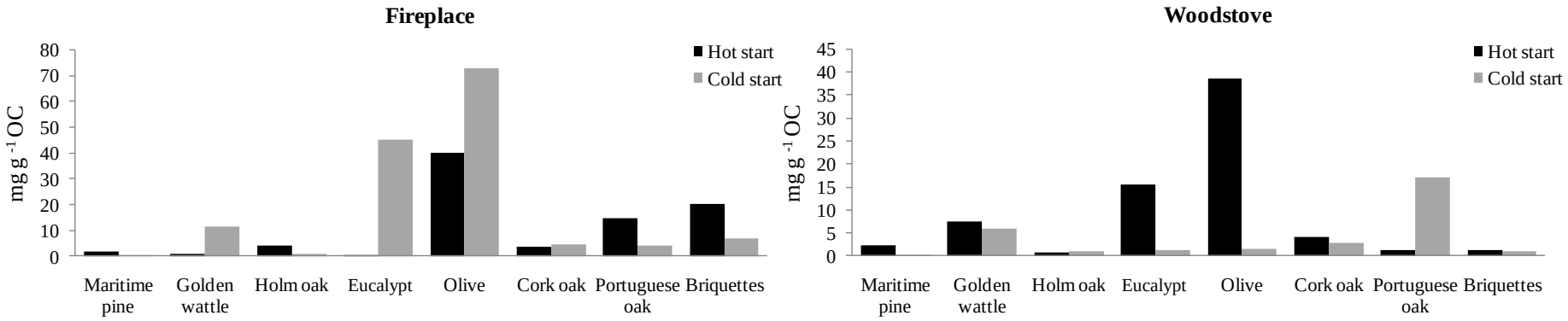

Figure 3.5 OC-normalised concentrations of Σ alcohols in the $PM_{2.5}$ from the various biomass fuels.

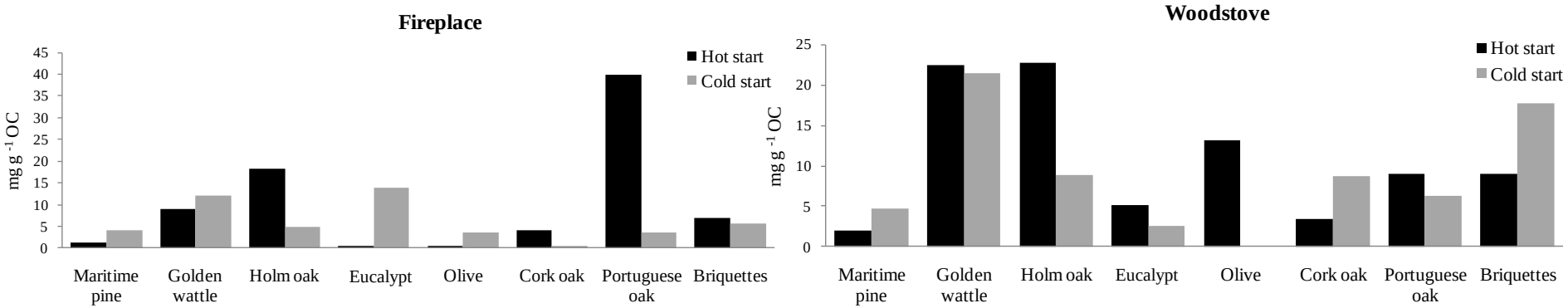

Figure 3.6 OC-normalised concentrations of Σ alkanoic acids in the $PM_{2.5}$ from the various biomass fuels.

Dicarboxylic acids were represented by an incomplete homologous series from C_3 to C_{16}. The C_{max} was observed for heptanedioic acid in a concentration range from 0.28 mg g^{-1}OC (woodstove with cold start – cork oak) to 10.2 mg g^{-1}OC (fireplace with hot start – Holm oak). Dicarboxylic acids in the same carbon range have been detected previously in the emissions from residential wood burning (Fine et al., 2004; Gonçalves et al., 2010) and from wildfires (Alves et al., 2010, 2011a; Kundu et al., 2010). Average concentrations of total dicarboxylic acids in $PM_{2.5}$ samples collected during the burning season in Amazonia were 2-8 times higher than those reported in urban aerosols (Kundu et al., 2010). However, dicarboxylic acids are ubiquitous compounds that can be generated from several primary sources or secondary processes and, thus, cannot be regarded as biomass burning tracers. Some alkyl esters of acids were detected in minor amounts, with a range from 0.02 mg g^{-1}OC (fireplace with hot start – eucalypt) to 1.40 mg g^{-1}OC (fireplace with cold start – maritime pine).

It should be noted that a significant fraction of other acids, whose individual characterisation was not possible, have a large contribution to the OC of smoke particles. Those other acids are mostly dicarboxylic acids and related compounds (e.g. ketocarboxylic acids) (Kundo et al., 2010), hydroxy-acids (e.g. glycolic acid) and oxo-acids (e.g. levulinic acid).

3.3.2.2 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds that is formed during incomplete combustion. More than twenty PAHs were identified in the smoke samples. It is difficult to draw firm conclusions about the relative PAH content in emissions resulting from cold or hot start combustions. The total OC-normalised concentrations of all PAHs (ΣPAHs) were in the range 1.47–10.7 mg g^{-1}OC for fireplace with hot start, 4.05–27.6 mg g^{-1}OC for fireplace with cold start, 2.27–29.3 mg g^{-1}OC for woodstove with hot start and 3.12–23.3 mg g^{-1}OC for woodstove with cold start (Figure 3.7). Emissions from the woodstove at higher temperatures possess a higher PAH content than those of the fireplace. Comparable average total PAH emissions were obtained in the woodstove and fireplace tests with cold start (~8.8 mg g^{-1}OC). The influence of these two parameters could explain the results. It is known that PAH amounts increase with the increase of temperatures (Lu et al., 2009; and references therein). On the other hand, it is

also observed that total PAH emissions increase with the increase of O_2 content in supplied air (Lu et al., 2009). In the present study, the fireplace operated at lower temperatures than those in the woodstove, but the O_2 content in supplied air was around 20%, while values lower than 15% were provided to the woodstove.

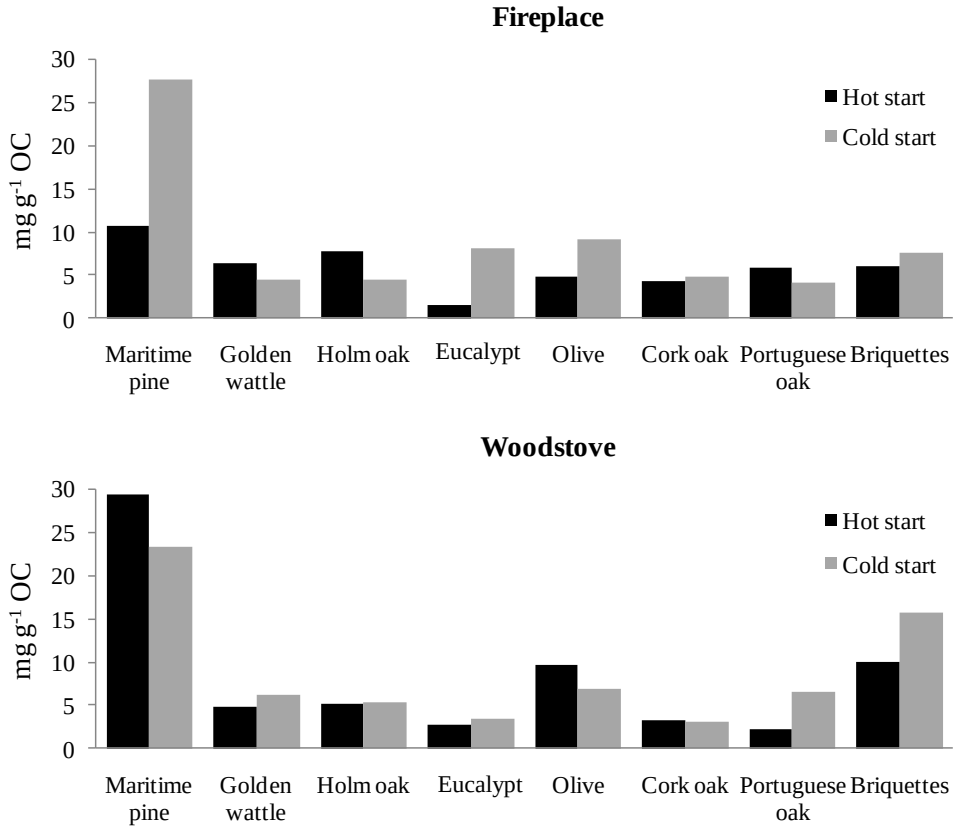

Figure 3.7 OC-normalised concentrations of Σ PAHs in the $PM_{2.5}$ from the various biomass fuels.

The PAH emissions from pine combustion were significantly higher than those of the other wood types, especially in emissions from woodstove. A great inter-study variation for the PAH content in emissions from burning pine species has been reported. This variation may be due to the large concentration range of flammable resin in the different pine woods tested (Gullet et al., 2003). Retene was the dominant aromatic hydrocarbon found in the softwood smoke (maritime pine – 6.43 mg g^{-1}OC for fireplace with cold start; 15.4 mg g^{-1}OC for woodstove with hot start) (Figure 3.8), whilst it was present at very small levels in the hardwood combustion emissions. Retene is the fully aromatised thermal alteration product of the resin acids present in conifer woods (Ramdahl et al., 1983).

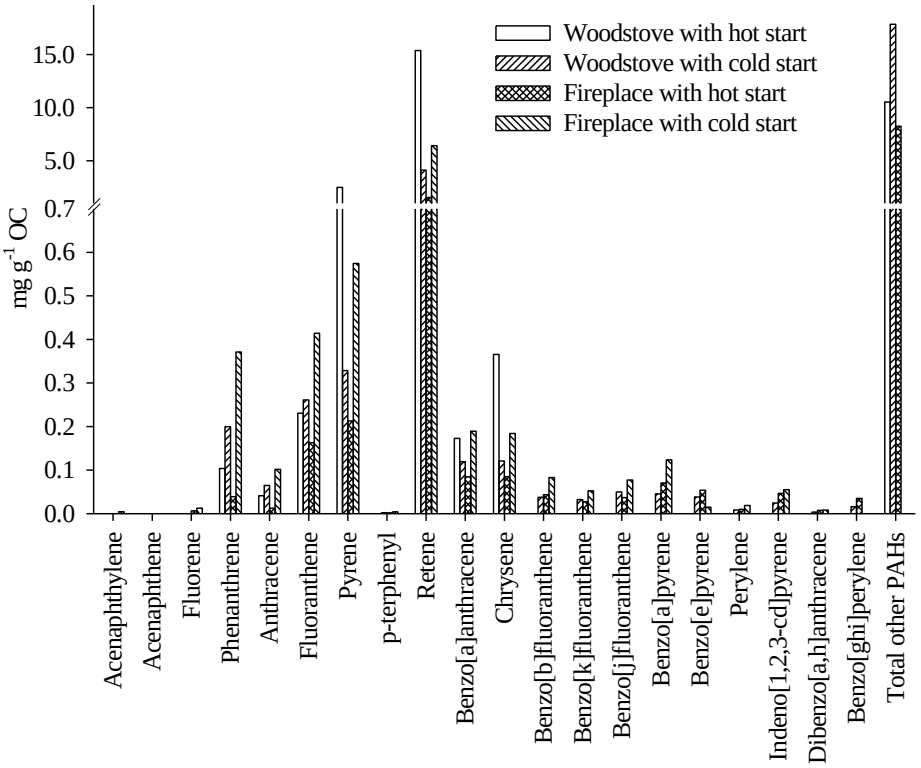

Figure 3.8 OC-normalised concentrations of PAHs in the $PM_{2.5}$ from Maritime pine.

The very high proportion of retene in softwood smoke was also verified by Fine et al. (2004b) in $PM_{2.5}$ emissions resulting from the combustion of USA prevalent trees (red maple, Douglas fir, white oak and loblolly pine) in a catalyst-equipped woodstove. In the smoke from these American wood species, retene represented 0.008–0.018 and 1.987–3.893 mg g^{-1}OC for hardwood and softwood, respectively. In this study, besides retene, fluoranthene, pyrene, and phenanthrene were the most prevalent PAHs found in both hardwood and softwood smoke. Because the major PAHs in wood smoke are generally the same as from other anthropogenic combustion emissions, diagnostic ratios are used for assessing the contribution of different sources (Alves, 2008). The IcdP/(BghiP+IcdP), BFs/BghiP, Flu/(Flu+Pyr) and BeP/(BeP+BaP) ratios are listed and compared with those of other sources in Table 3.3. In general, the diagnostic ratios can be differentiated from those of other combustion sources. The Flu/(Flu+Pyr) ratios of 0.40±0.09 and 0.42±0.04 for woodstove and fireplace, respectively, are below the values reported for broad-leaf tress, shrubs, grasses and cereal straw (Hays et al., 2005; Oros et al., 2006; Wang et al., 2009).

Table 3.3 PAH diagnostic parameters.

					Woodstove	
			Flu/(Flu+Pyr)	**IcdP/(BghiP+IcdP)**	**BFs/BghiP**	**BeP/(BeP+BaP)**
This study	Maritime pine	Hot start				
		Cold start	0.44	0.60	7.51	0.46
	Golden wattle	Hot start	0.38	0.57	4.00	0.46
		Cold start	0.45	0.59	4.91	0.40
	Holm oak	Hot start	0.44	0.60	5.09	0.50
		Cold start	0.44	0.55	4.47	0.41
	Eucalypt	Hot start	0.46	0.58	3.41	0.43
		Cold start	0.44	0.53	3.75	0.40
	Olive	Hot start	0.18	0.73	38.1	0.57
		Cold start	0.45	0.54	6.23	0.49
	Cork Oak	Hot start	0.20	0.69	42.4	0.52
		Cold start	0.37	0.58	5.03	0.38
	Portuguese oak	Hot start	0.45	0.57	3.83	0.47
		Cold start	0.42	0.57	4.75	0.38
	Briquettes	Hot start	0.47	0.57	8.28	0.61
		Cold start	0.46	0.57	5.98	0.48
					Fireplace	
	Maritime pine	Hot start	0.43	0.57	3.08	0.43
		Cold start	0.42	0.58	5.26	0.11
	Golden wattle	Hot start	0.48	0.59	3.10	0.45
		Cold start	0.39	0.59	4.90	0.42
	Holm oak	Hot start	0.41	0.57	4.40	0.40
		Cold start	0.39	0.61	6.16	0.40
	Eucalypt	Hot start	0.45	1.00		0.47
		Cold start	0.44	0.57	4.29	0.44
	Olive	Hot start	0.46	0.60	6.69	0.46
		Cold start	0.36	0.59	3.77	0.38
	Cork Oak	Hot start	0.49	0.58	3.60	0.43
		Cold start	0.39	0.57	4.09	0.44
	Portuguese oak	Hot start				
		Cold start	0.35	0.54	3.14	0.41
	Briquettes	Hot start	0.44			0.48
		Cold start	0.47	0.64	7.86	0.49

Wang et al., 2009	Broad-leaf trees	0.50 - 0.55			
Wang et al., 2009	Shrubs	0.54 - 0.60			
Oros et al., 2006	Grasses	0.53 - 0.63			
Hays et al., 2005	Cereal straw	0.50 - 0.53	0.52 - 1.0		
Chen et al., 2004	Coal	0.48	0.43	1.86	0.91
Rogge et al., 1993	Noncatalyst-equip. vehicles	0.61	0.04	0.58	
Rogge et al., 1993	Catalyst-equip. vehicles	0.44	0.09	1.16	

Flu – Fluoranthene; Pyr – Pyrene; IcdP – Indeno[1,2,3-cd]pyrene; BghiP – Benzo[ghi]perylene; BFs – Benzofluoranthenes ; BeP – Benzo[e]pyrene; BaP - Benzo[a]pyrene

The values of this diagnostic ratio can be differentiated from those of other combustion sources, such as vehicular exhausts and coal combustion, which are slightly higher (Chen et al., 2004; Rogge et al., 1993). The BFs/BghiP ratio was 5.2±1.5 and 4.6±1.5 for woodstove and fireplace, respectively. The comparatively high values for olive and cork oak for woodstove with hot start were not included in the average calculation. The high BFs/BghiP ratios obtained for olive (38.14) and cork oak (42.40) are due to the very low concentrations of BghiP in the smoke of these two wood species. The values of this diagnostic ratio can be distinguished from those of other combustion sources, such as vehicular exhausts and coal combustion, which have lower values (Chen et al., 2004; Rogge et al., 1993). The IcdP/(BghiP+IcdP) ratio was 0.59±0.05 and 0.61 ± 0.11 for woodstove and fireplace, respectively. Much lower values have been obtained for vehicular emissions (Rogge et al., 1993) and coal combustion (Chen et al., 2004). The BeP/(BeP+BaP) ratios were 0.46±0.07 and 0.41±0.01 for woodstove and fireplace, respectively. These values differ from the higher ratio produced by coal combustion.

3.3.2.3 Phenolic compounds

Phenolic compounds included polyphenols, methoxyphenols and alkyl phenols. Methoxyphenols have been identified as prominent lignin thermal degradation products and as semi-volatile components of smoke particles (Hawthorne et al., 1988). These products can be classified, as regards to their origin, into three general groups: coumaryl, vanillyl or guaiacyl and syringyl compounds (Simoneit et al., 1993) (Table 3.4).

Table 3.4 OC-normalised concentrations of the most abundant phenolic compounds in the emissions from the various biomass fuels (mg g^{-1}OC).

		Vanillic acid	Syringic acid	Coniferyl alcohol	Catechol	Methylcatechol	Pyrogallol	Vanillin
Woodstove								
Maritime pine	Hot start	1.72	0.126	0.0176	4.21	3.38	2.22	2.59
	Cold start	14.8	0.233	0.355	18.9	18.2	3.56	8.34
Golden wattle	Hot start	1.46	2.74	0.956	27.7	19.6	3.43	5.81
	Cold start	3.72	2.23	0.946	23.7	29.7	29.6	65.2
Holm oak	Hot start	1.83	8.55	0.583	25.8	12.4	5.57	12.3
	Cold start	5.45	11.4	0.535	16.8	17.6	32.7	5.64
Eucalypt	Hot start	1.02	6.73	0.129	26.1	11.1	59.2	3.33
	Cold start	1.37	8.72	0.311	---	9.04	25.8	4.90
Olive	Hot start	2.66	5.30	1.52	4.63	2.98	---	8.38
	Cold start	+	+	3.14	+	---	+	6.89
Cork oak	Hot start	1.34	4.93	0.756	34.0	37.3	59.7	7.09
	Cold start	7.44	14.2	1.49	24.1	13.1	29.0	7.56
Portuguese oak	Hot start	2.66	10.6	0.511	35.2	34.0	50.9	7.02
	Cold start	3.84	12.5	0.188	48.2	34.2	110	6.53
Briquettes	Hot start	9.52	20.9	---	15.6	6.05	---	---
	Cold start	17.7	34.8	1.33	38.7	51.9	77.5	13.0
Fireplace								
Maritime pine	Hot start	0.553	+	0.759	2.25	3.41	0.842	3.94
	Cold start	3.46	0.0665	1.26	15.0	25.3	2.73	---
Golden wattle	Hot start	1.68	3.91	1.79	26.0	25.8	5.73	---
	Cold start	1.32	2.90	3.15	10.1	18.9	22.1	6.47
Holm oak	Hot start	5.14	22.1	7.66	16.8	13.8	23.3	14.0
	Cold start	2.41	9.63	1.13	19.0	10.2	38.7	5.36
Eucalypt	Hot start	1.25	12.8	0.143	16.7	9.88	70.9	---
	Cold start	2.94	19.2	0.418	64.8	50.6	88.9	10.8
Olive	Hot start	0.811	2.06	0.829	6.21	6.33	12.3	17.3
	Cold start	1.41	2.16	4.85	11.6	9.57	29.0	5.67
Cork oak	Hot start	1.59	5.41	2.03	29.2	20.8	37.7	8.18
	Cold start	0.694	2.42	4.11	8.97	8.71	29.5	24.7
Portuguese oak	Hot start	1.53	8.16	0.681	36.9	24.2	53.1	11.2
	Cold start	3.05	8.46	2.94	14.7	13.6	28.3	14.0
Briquettes	Hot start	8.84	12.9	0.268	32.0	23.4	40.7	16.2
	Cold start	10.1	8.54	0.673	38.2	18.5	36.6	6.65

(---) not detected; (+) detected, but not quantified, because of abundances close to the detection limit.

Softwood smoke contains 4-hydroxy-3-methoxyphenyl (guaiacyl or vanillyl) compounds, whereas hardwood burning contributes mainly to the formation of 4-hydroxy-3,5-dimethoxyphenyl (syringyl) compounds because of a different lignin structure. These compounds were emitted in higher amounts by woodstove with cold start (10.6 to 236.5 mg g^{-1}OC) and by fireplace with cold start (47.8 to 242.1 mg g^{-1}OC) (Table 3.4). The predominant methoxyphenols found in the smoke were the vanillic and syringic acids. Vanillic acid was emitted in higher amounts by pine (softwood) than by hardwood species, while the opposite was observed for syringic acid. Vanillin, catechol, methylcatechol and pyrogallol are other phenolic compounds that are quite impressive in the smoke of all species.

3.3.2.4 Other biomarkers

Phytosterols, terpenoids, including resin acids, and saccharides represent biomarker constituents in the smoke from residential wood combustion. The most abundant phytosterol in all smoke samples was *β*-sitosterol, followed by stigmasterol, at lower abundances. The high *β*-sitosterol normalised-OC concentrations in maritime pine (fireplace with hot start – 39.9 mg g^{-1} OC) emissions deserve consideration. However, as *β*-sitosterol emissions vary greatly with wood species, it cannot be regarded as a candidate to separate hardwood from softwood combustion emissions in source apportionment studies. Stigmasterol was only present in the smoke of hardwood species. This result is in accordance with the study by Fine et al. (2004b). Thus, stigmasterol may be pointed out as a potential tracer for the smoke from deciduous trees. Several products from the thermal alteration of sterol precursors were identified (e.g. stigmastan-4,5,22-triene, and stigmastan-3,5,22-triene). Among these, the most abundant was stigmastan-3,5-diene. Some terpenoids were also found, mostly in trace amounts, except lupeol that appeared with great expression in maritime pine $PM_{2.5}$ emissions (4.73 mg g^{-1}OC). Resin acids, such as isopimaric, dehydroabietic and pimaric acids, were detected as significant components of softwood emissions, but were found only in trace quantities in the emissions from hardwoods (Table 3.5).

Table 3.5 OC-normalised concentrations of resin acids in the emissions from the various biomass fuels (mg g^{-1}OC).

		Dehydroabietic acid	Isopimaric acid	Pimaric acid	Abietic acid
		Woodstove			
Maritime pine	Hot start	83.1	4.71	94.8	+
	Cold start	154	30.9	198	12.0
Golden wattle	Hot start	1.18	0.466	2.75	0.0661
	Cold start	21.2	3.41	26.9	7.81
Holm oak	Hot start	0.779	---	0.779	+
	Cold start	12.3	1.94	15.1	0.264
Eucalypt	Hot start	2.74	---	2.74	0.00778
	Cold start	1.62	0.524	2.14	0.460
Olive	Hot start	0.504	0.165	0.669	+
	Cold start	5.43	0.982	6.41	3.25
Cork oak	Hot start	0.385	0.0630	0.448	0.0151
	Cold start	15.9	5.61	26.0	11.7
Portuguese oak	Hot start	0.256	0.118	0.374	0.00859
	Cold start	25.5	2.25	30.8	1.60
Briquettes	Hot start	7.60	2.26	10.6	0.0390
	Cold start	21.5	5.88	29.3	0.429
		Fireplace			
Maritime pine	Hot start	67.9	10.3	80.0	9.07
	Cold start	306	37.7	355	29.4
Golden wattle	Hot start	6.23	1.03	8.51	---
	Cold start	---	0.631	0.631	0.515
Holm oak	Hot start	---	0.305	0.305	---
	Cold start	0.659	0.0472	0.706	---
Eucalypt	Hot start	1.29	0.748	2.05	---
	Cold start	26.6	1.80	28.5	---
Olive	Hot start	---	0.451	0.754	1.13
	Cold start	8.14	0.860	9.00	---
Cork oak	Hot start	---	0.117	0.471	---
	Cold start	1.24	---	1.24	0.285
Portuguese oak	Hot start	50.9	2.79	53.7	1.47
	Cold start	1.13	0.462	1.59	0.235
Briquettes	Hot start	6.53	3.54	10.1	---
	Cold start	13.7	3.19	18.5	---

(---) not detected; (+) detected, but not quantified, because of abundances close to the detection limit.

Isopimaric and pimaric acids are primary natural products occurring as such in resins, while dehydroabietic acid is an oxidative alteration product from other resin acids (Simoneit et al., 2000). These constituents were emitted at higher concentrations in cold start tests, independently from the burning appliance used. In addition to differences related to the presence or absence of ducts filled with resin and distinct combustion temperatures, moisture may play an important role in the abundance of the resin acids as compared to other carbonaceous species (Mazzoleni et al., 2007).

The major organic components of smoke particles from biomass burning were monosaccharide derivatives from the breakdown of cellulose and hemicelluloses, such as levoglucosan, mannosan and galactosan (Simoneit et al., 1999). In general, these compounds were emitted in larger amounts by the woodstove with hot start and by the fireplace with cold start (Table 3.6).

As expected, levoglucosan, a specific marker for wood combustion in ambient PM samples (Fine et al., 2004a; Schmidl et al., 2008a), was the most abundant organic compound (Table 3.6). The global amounts of anhydrosugars were generically higher in the smoke resulting from experiments with hot start than those obtained at lower combustion temperatures. While the average values for the hot start tests were 426 mg g^{-1} OC (fireplace) and 466 mg g^{-1} OC (woodstove), the corresponding values for cold start tests were 379 and 415 mg g^{-1} OC. However, for the majority of biofuels, the levoglucosan emissions were usually higher for the hot woodstove tests (average = 383 mg g^{-1} OC) at higher temperatures and for the fireplace with cold start (average = 278 mg g^{-1} OC).

Mannosan was the second most abundant anhydrosugar product from the hemicellulose pyrolysis. Galactosan was the third most abundant anhydrosugar in the wood smoke samples. Levoglucosan, mannosan, and galactosan were emitted in varying ratios, probably due to differences in the relative content of cellulose and hemicellulose in different biofuels (Engling et al., 2006). Biomass pyrolysis products are a complex combination of the products from the individual pyrolysis of cellulose, hemicellulose, and extractives, each of which has its own chemical degradation pathways. In addition, secondary reaction products result from cross-reactions of primary pyrolysis products and between pyrolysis products and the original feedstock molecules (Mohan et al., 2006).

Table 3.6 OC-normalised concentrations of sugars in the emissions from the various biomass fuels (mg g^{-1}OC).

		Galactosan	Mannosan	Levoglucosan	Other sugars	L/M
		Woodstove				
Maritime pine	Hot start	114	232	335	35.0	1.44
	Cold start	81.8	237	291	140	1.23
Golden wattle	Hot start	56.0	42.3	374	206	8.85
	Cold start	48.6	115	159	147	1.39
Holm oak	Hot start	34.9	12.5	205	70.4	16.5
	Cold start	40.8	81.2	126	150	1.55
Eucalypt	Hot start	94.6	66.6	463	170	6.95
	Cold start	23.3	289	+	83.6	
Olive	Hot start	19.4	30.1	99.2	199	3.30
	Cold start	+	+	+	---	
Cork oak	Hot start	53.1	52.9	293	77.4	5.53
	Cold start	53.0	108	241	88.5	2.23
Portuguese oak	Hot start	65.2	+	349	190	
	Cold start	125	320	506	216	1.58
Briquettes	Hot start	226	31.9	948	307	29.7
	Cold start	191	293	410	284	1.40
		Fireplace				
Maritime pine	Hot start	37.6	108	148	83.4	1.37
	Cold start	170	+	378	345	
Golden wattle	Hot start	41.4	91.5	301	293	3.29
	Cold start	35.2	15.9	101	113	6.35
Holm oak	Hot start	38.7	15.2	106	51.0	7.00
	Cold start	66.0	26.9	186	82.4	6.93
Eucalypt	Hot start	98.1	45.9	506	274	11.0
	Cold start	177	61.3	582	402	9.49
Olive	Hot start	24.4	23.5	79.6	96.8	3.39
	Cold start	30.7	58.1	133	65.7	2.28
Cork oak	Hot start	44.7	26.4	184	87.5	6.98
	Cold start	25.9	15.2	112	44.3	7.35
Portuguese oak	Hot start	50.3	91.0	327	166	3.60
	Cold start	55.7	+	199	177	
Briquettes	Hot start	133	85.4	+	484	
	Cold start	183	265	532	192	2.01

(---) not detected; (+) detected, but not quantified, because of abundances close to the detection limit.

Pyrolysis of each constituent is itself a complex process that is dependent of many factors, rendering difficult the attainment of simple relationships between the combustion temperature and the amounts of products in the smoke. It is known that cellulose degradation occurs at 240–350ºC to produce anhydrocellulose and levoglucosan, while hemicelluloses decomposes at temperatures of 200–260ºC, yielding more volatiles, less tars, and less chars than cellulose (Mohan et al., 2006). However, in slow pyrolysis, the loss of hemicelluloses of wood starts taking place at temperatures from 130 to 194ºC, which are in the range of values registered in the cold start tests in the fireplace. Most hemicelluloses do not give rise to significant amounts of levoglucosan (Mohan et al., 2006), although the slow pyrolysis of some hemicellulosic constituents of wood could result in the formation of the carbohydrate as a main product (Aho et al., 2008).

The relative proportions of levoglucosan to mannosan (L/M) have been used for source reconstruction of combustion derived by-products in atmospheric aerosols. For example, inputs from very specific poor-quality brown coals gave L/M ratios greater than 50 in atmospheric aerosols (Fabbri et al., 2009). Differences in the L/M ratio in smoke from softwood and hardwood/grass combustion (~5 versus ~10–20, respectively) can further support discrimination between inputs from these combustion sources to the atmosphere (Louchouarn et al., 2009; and references therein). Herbaceous tissues can produce relatively high L/M ratios, in the range from 25 to 50 (Engling et al., 2009). In the present study, lower ratios than those reported for soft- and hardwood smoke were obtained. In addition to differences in the cellulosic content of the different biofuels, the emission of saccharidic compounds may strongly depend on combustion characteristics that are not well-understood. Under controlled combustion conditions (150–1050 °C), Kuo et al. (2008) determined the levoglucosan content in samples from 3 wood species. The anhydrosugar was only detectable in low temperature samples (150–350°C), with maximum yield obtained from samples produced at 250°C, regardless of plant species. A laboratory emission study of wood and pellet boilers gave 0.3% w/w to 22% w/w levoglucosan to particle mass, indicating that the levoglucosan fraction may be highly dependent on combustion parameters, making it uncertain to use it as a quantitative tracer under real-world burning conditions (Hedberg et al., 2006). Another variable that has a strong influence on the yield of levoglucosan from cellulose is the presence of inorganic ions (Dobele et al., 2005). It has been observed that the presence of mineral matter in wood

decreases the temperature of cellulose pyrolysis (Williams and Horne, 1994). Thus, quantitative estimates of wood burning inputs to atmospheric particles will be very doubtful using exclusively levoglucosan as a tracer.

Other saccharidic compounds included inositol, glycerol among others, especially in the smoke from briquettes and eucalypt.

3.4 Conclusions

The traditional Portuguese burning appliances tested in this study present higher $PM_{2.5}$ emission factors, a lower EC content of the fine particle mass, and a higher OC mass fraction compared to those described in the literature for the residential wood combustion in countries where certification of stoves is required to meet certain emission limits. In Portugal, the certification process is still in progress and, therefore, catalytic elements in the woodstove designs or high-efficiency woodstoves that reduce emissions by careful control of air flow and temperature are not common.

This work provides detailed information on organic composition of smoke particles from residential combustion of the most prevalent Portuguese woods in an attempt of contributing with new data for source apportionment methodologies. Two types of residential biomass combustion appliances were tested: woodstove and fireplace. In order to evaluate the influence of temperature on the combustion flue emissions characteristics, two sets of experiments were performed for each wood fuel type: cold start and hot start. Some differences between particle emissions from softwood and hardwood burning were observed. Maritime pine, the only softwood studied, was the wood species that contributed to the lowest $PM_{2.5}$ emission in both fireplace and woodstove. In general, the $PM_{2.5}$ emissions were higher during the experiments with cold start. Concerning the carbonaceous content of $PM_{2.5}$, maritime pine produced the highest EC emissions (fireplace and woodstove), while Holm oak and briquettes presented the lowest EC content in $PM_{2.5}$ from fireplace. For woodstove, the golden wattle smoke encompassed the lowest EC emissions. The OC content did not show appreciable differences between species, combustion appliances or combustion temperatures. In general, high OC/EC ratios were obtained for all species, especially in the fireplace. The lowest OC/EC ratios were obtained for the maritime pine. Alkanes, PAHs, ketones, alkanols, resin acids and alkyl esters of acids were emitted in large concentrations in cold start tests, independently of the burning

appliance used. Alkenes and anhydrosugars were emitted in higher amounts by the woodstove with hot start and by fireplace with cold start. Phenolic compounds were emitted in highest concentration by woodstove with cold start and by fireplace with cold start. The major organic components in particles from biomass burning were anhydrosugars, in particular levoglucosan, acids and aliphatic compounds. Retene was the dominant aromatic hydrocarbon found in the softwood smoke, whilst it was present at very small levels in the hardwood combustion emissions. Guaiacyl, like vanillic acid, and synapyl compounds were identified in softwood smoke, whereas hardwood burning contributed mainly to the formation of syringyl compounds, such as syringic acid. Stigmasterol was only present in the smoke of hardwood species; thus, this compound may be pointed out as a potential tracer for smoke from deciduous trees. β-Sitosterol has a great expression in the smoke of softwood species. However, as β-sitosterol emissions vary greatly with wood species, it cannot be regarded as a candidate to separate hardwood from softwood combustion emissions in source apportionment studies. Since important differences between hardwood and softwood combustion were seen among the substituted phenols, aromatic compounds and phytosterols, composite emission profiles, weighted based on the estimated usage of the distinct wood types, should be accounted for in chemical mass balance models that use organic compounds as tracers. Weighted composite residential wood combustion source profiles based on the woodstove and fireplace usage patterns in a particular region should also be developed for further mass balance calculations, which attempt to determine the contribution of wood smoke sources to ambient fine particle samples.

Taking into account that the distributions and abundances of the biomass smoke constituents are dependent on combustion temperature, the emission profiles obtained in this study should not be used as absolute but as relative chemical fingerprints for residential wood burning. Besides differences in combustion temperatures and biofuel types, the variability in emission profiles may be due to several factors, including differences in fuel array and configuration, composition and dimensions of branches and bark, fuel moisture content, flame temperature, aeration, or the presence of other constituents (e.g. acids, bases, or salts, either catalysing or inhibiting the formation of certain combustion products). Future studies would require a more strict control of these variables and more replicate burning tests.

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CHAPTER 4

Chapter 4. Fireplace and woodstove fine particle emissions from combustion of western Mediterranean wood types

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Abstract

Wood from seven species of trees grown in the Portuguese forest (*Pinus pinaster, Eucalyptus globulus, Quercus suber, Acacia longifolia, Quercus faginea, Olea europea* and *Quercus ilex rotundifolia*), and briquettes produced from forest biomass waste were burned in a fireplace and in a woodstove to determine the chemical composition of fine particle ($PM_{2.5}$) emissions. Samples were analysed for organic and elemental carbon (OC/EC), water soluble ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-}) and 67 elements. The $PM_{2.5}$ emission factors (g kg^{-1} fuel burned, dry basis) were in the ranges 9.9-20.2 and 4.2-16.3, respectively, for the fireplace and the woodstove. Organic carbon contributed to about 50% of the fine particle mass in the emissions from every wood species studied in both burning appliances. The carbonaceous component of $PM_{2.5}$ was dominated by organic carbon, accounting for more than 85% of the total carbon (TC): OC/TC ranged from 0.85 to 0.96 (avg. 0.92) for the fireplace and from 0.86 to 0.97 (avg. 0.93) for the woodstove. The water-soluble ions accounted for 0.64 to 11.3% of the $PM_{2.5}$ mass emitted from the fireplace, whereas mass fractions between 0.53 and 13.6% were obtained for the woodstove. The golden wattle wood smoke showed a much higher ionic content than the emissions from the other wood types. Trace elements represented 0.4 to 2.5% and 0.2 to 2.2% of the $PM_{2.5}$ mass emitted, respectively, from the fireplace and the woodstove, which corresponded to average total emissions of 132±77.3 mg kg^{-1} and

93.4±60.8 mg kg^{-1} of wood burned. Among these, K, Pb, Al, Mn and Sr were present in all samples. From the emission profiles of the individual experiments, composite wood combustion profiles are suggested with the aid of a cluster analysis.

Keywords: woodstove, fireplace, $PM_{2.5}$, biomass burning, water-soluble ions, metals, OC/EC.

4.1 Introduction

Residential wood burning is known to be a significant source of particulate matter in many regions worldwide (Bari et al., 2009; Caseiro et al., 2009; Favez et al., 2009; Jeong et al., 2008; Jiang and Bell, 2008; Ristovski et al., 2010; Ryu et al., 2007). The use of biomass fuels is becoming increasingly important in accordance with the effort to restrict the emissions of greenhouse gases and also due to the rising cost of oil. Biomass burning particles are efficient cloud condensation nuclei (CCN) and can influence the formation of precipitation (Reid et al., 2005; Reutter et al., 2009; Rose et al., 2010; Rosenfeld et al., 2008). Biomass burning is also a source of radiactively active carbon-containing particles (Langmann et al., 2009; Ramanathan et al., 2001), which encompass several toxic constituents, including carcinogenic and/or mutagenic compounds, such as polycyclic aromatic hydrocarbons (PAHs). Is has been observed that the total PAH content is higher for combustion particles from wood smoke as compared to vehicle exhaust (Kocbach et al., 2006). There is also strong evidence that acute respiratory infections, chronic obstructive pulmonary disease and other respiratory conditions are associated with indoor biomass smoke (Torres-Duque et al., 2008). Wood smoke particles seem to affect factors such as inflammation and blood coagulation, supposed to be involved in cardiovascular morbidity and mortality (Barregard et al., 2006). Several studies have been carried out to characterise the organic composition of the particulate emissions from residential wood combustion (Fine et al., 2004a,b; McDonald et al., 2000; Schauer et al., 2001; Schmidl et al., 2008). However, the profiles of inorganic constituents are still unavailable since only a small number of metals and water-soluble ions have been determined in a few studies (Gonçalves et al., 2010; Schauer et al., 2001; Schmidl et al., 2008), and the effects of different combustion techniques and fuels have not been considered. The combustion-related trace elements and water-soluble ions are biogeochemically active species, including in nutrient cycling (Baker et al., 2006, Furutani et al., 2010). It is also known that the metal fraction may represent a substantial portion of the toxicity of aerosol particles (Linak and Wendt, 1993). As trace elements associated with finer particles are non-volatile in nature, they are less prone to chemical transformations and remain in the form as they were emitted, despite the fact that they tend to undergo long range atmospheric transport (Kulshrestha et al., 2009). Receptor models attempting to apportion the ambient pollution

levels attributed to biomass burning have been using compounds such as non mineral potassium as a tracer. However, potassium is also emitted by other major sources such as meat charbroiling (Schauer et al., 1999) and refuse incineration (Sheffield et al., 1994) and, therefore, cannot be used as a sole wood smoke tracer in source apportionment calculations.

If source-apportionment methods are to be applied at the national scale, detailed fireplace and woodstove combustion source profiles must be determined for all of the important wood types burned. The current study aims to make an in-depth characterisation of particulate compound emissions, with a focus on the screening of inorganic constituents, from the residential combustion of a wide variety of Portuguese biomass fuels. Additional information concerning the detailed organic speciation of the smoke particles can be found elsewhere (Gonçalves et al., 2011). The differences in emissions that occur when different woods or burning appliances are used can possibly be employed to resolve ambient fine particle contributions from residential biomass burning and, thus, from the specific geographic regions where those species are burned. In addition, to provide a credible accounting of pollution sources, emission inventories need to include residential wood combustion. Hence, this study will also contribute to improve emission inventories.

4.2 Methodology

Two types of residential biomass combustion appliances were selected for the source tests: i) a cast iron woodstove (Solzaima, model Sahara), operated manually in batch mode and with handheld control of combustion air (primary air underbed feed), and ii) a traditional Portuguese brick open fireplace operated manually in batch mode and with no control of combustion air. The wood from the seven most prevalent tree species in Portugal and commercial briquettes (Table 4.1) were chosen for the combustion tests. Briquettes were made of wastes from forest cleaning activities and/or from local wood processing industries, but their exact composition was not provided by the manufacturer. Mechanical piston-presses were used to produce the cylindrical briquettes 20 cm in length and 7 cm in diameter. During each combustion experiment, which lasted between 45 and 90 minutes, about 6 kg of wood were burned, using three consecutive batches of around 2 kg each. The wood was burned as split logs of 30-50 cm in length and around 10 cm in diameter. Fires

were ignited with pine cones and small kindling pieces cut from the same wood being burned. Three or four combustion experiments have been performed for each biofuel type.

Table 4.1 Biomass characteristics.

		Proximate analysis (% wt, as received)	**Ultimate analysis (% wt, dry basis)**					
Common name	**Scientific name**	**Moisture**	**C**	**H**	**N**	**S**	**O***	**Ash**
Maritime pine	*Pinus pinaster*	9.10	51.40	6.20	0.16	ND	41.88	0.36
Eucalypt	*Eucalyptus globulus*	11.30	48.60	6.20	0.16	ND	44.28	0.75
Cork oak	*Quercus suber*	12.20	51.61	6.03	0.18	ND	40.76	1.41
Golden wattle	*Acacia longifolia*	8.40	50.83	6.43	0.18	ND	41.80	0.75
Olive	*Olea europea*	15.50	53.56	7.68	0.18	ND	36.64	1.94
Portuguese oak	*Quercus faginea*	14.10	50.26	7.32	0.19	ND	41.85	0.38
Holm oak	*Quercus ilex*	8.70	50.61	7.14	0.18	ND	39.75	2.32
Briquettes	---	8.40	50.76	7.01	0.16	ND	41.16	0.91

ND – not detected because the concentration was below the detection level of 0.01%wt; * By difference.

The first one included the start-up phase after a batch of wood logs had been added. The other tests included the intermediate and burn-out phases. They were initiated with the load of a batch of fuel to the combustion chamber already at a temperature of around 100ºC and with the presence of a small amount of burning char. These tests continued until the CO_2 concentrations in the flue gases (i.e., combustion intensity) started to decrease and the burn-out phase with increased CO emissions became predominant. The burn-out phase was considered to continue until the CO_2 concentrations in the flue gases reached 4%. In this paper, the emissions from the cold start, i.e., initial kindling wood batch, were not included since this phase is limited to just a few minutes, whereas flaming and glowing conditions predominate for several hours in "ordinary" domestic operation. Temperatures in the combustion chamber of the woodstove in the range 200–725ºC, but generally from 240 to 450ºC, corresponded to temperatures at the top of the chimney from 100ºC to 275ºC. Except some peaks around 600ºC, temperatures in the combustion chamber of the fireplace were usually lower than 300ºC. As observed for the woodstove, a linear correlation between the temperatures in the combustion chamber and the temperature of the flue gases in the chimney was registered for the fireplace.

A detailed description of the combustion facility (configuration, operating control, etc.), as well the correlation between particle emission factors and CO, CO_2, O_2, fuel moisture content, combustion temperatures, burn rates, etc., can be found elsewhere (Calvo et al., 2011; Fernandes et al., 2011).

Collection of particulate matter with aerodynamic diameters below 2.5 μm ($PM_{2.5}$) was performed in a dilution tunnel, which is similar to other systems reported in previous studies (Boman et al., 2005; England et al., 2007a,b; Fine et al., 2004; Hedberg et al., 2002; Tissari et al., 2008). Dilution sampling is used to characterise particle emissions from combustion because it simulates the rapid cooling and dilution that occurs as exhaust mixes with the atmosphere (Lipsky and Robinson, 2005). The dilution tunnel consisted of a cylindrical tube with 0.20 m internal diameter and 11 m length. The dilution ratios applied to the flue gases from the woodstove were around 25:1. In the case of the fireplace, 4- to 5-times dilution ratios were applied. $PM_{2.5}$ were collected in the dilution tunnel using an Echo sampling head (TECORA, model 2.004.01, Italy) operating at a flow of 2.3 $m^3\ h^{-1}$, onto quartz fibre filters (47 mm diameter), previously fired at 500ºC for 4 h to eliminate organic contaminants. $PM_{2.5}$ was sampled in continuous during the combustion of a batch of fuel (combustion cycle). The temperature in the particle sampling point in the dilution tunnel was in the range 25–35ºC, and the relative pressure was maintained typically at 10 mm H_2O below the atmospheric pressure. The gas flow velocity was around 6.3 $m\ s^{-1}$. During each combustion experiment, the quartz filter was replaced 3 times, that is, 4 filters were used. Since each replacement took less than 1 minute, the overall particle emission factor for each combustion cycle was considered to not be significantly affected. Taking into account that at the entrance of the $PM_{2.5}$ sampling head, in the dilution tunnel, the gas velocity was below the velocity of the flue gas stream, some departure from isokinetic conditions were observed. Thus, the $PM_{2.5}$ emission factors should be considered as approximate values of the real ones. The particulate matter mass was obtained by gravimetric determination after 24 h equilibration of the filters in a conditioned room (20 ± 1°C, 50 ± 2% relative humidity). A microbalance (Sartorius M5P with range up to 1 g reading to ± 0.5 μg) was used for that purpose.

The carbonaceous content (OC and EC) of particulate matter collected on the quartz fibre filters was analysed using a thermal-optical transmission technique (Alves et al., 2010). For the determination of soluble inorganic ions, small parts of the filters were

extracted with ultra pure Milli-Q water. Dionex AS14 and CS12 chromatographic columns with Dionex AG14 and CG12 guard columns coupled to Dionex AMMS II and Dionex CMMS III suppressors, respectively for anions and cations, were used. The remaining parts of the filters were mixed with 10 ml of 10% nitric acid and then heated at a hot block setting of 110ºC for 1 hour. After cooling, internal standard solution was added and dilution was made to 50 g. Inductively coupled plasma mass spectrometry (ICP/MS) analyses were performed on the supernadant solutions using an Agilent instrument (7500 series). Data were collected for masses of 5–250 amu over a 1–2 minute period with sensitivity in the μg L^{-1} range for most elements. Samples were analysed for 67 elements, of which, around 20 elements were typically found at quantifiable levels. Blank filters were analysed simultaneously in the batches of their respective filter samples and the corresponding blank concentrations were subtracted for each sample. The detection limits were determined by the analysis of low level standards. By doing so, the precision of the entire response measurement system was measured, and a statistically valid 99% confidence limit could be calculated from the standard deviation of the response. Blank filters were also spiked with 31 elements at known concentrations to perform recovery tests. The percentage recoveries ranged from 94 to 102%. Not detected (ND) indicates that the analyte may be present below the detection limit.

4.3 Results and Discussion

4.3.1 Chemical composition of particle emissions

Varying emissions of $PM_{2.5}$ were observed in this study for different biomass fuels (Table 4.2). Except for blue gum in the fireplace, all the values are lower than the U.S. Environmental Protection Agency emission factor for residential combustion of 17.3 g of $PM_{2.5}$ kg^{-1} of wood burned (EPA, 1996). While some emission factors in the literature are comparable to our results (Fine et al., 2001; Purvis et al., 2000), some others are close to the lower limits obtained in this study (Gonçalves et al., 2010; Wardoyo et al., 2006). The fireplace was the combustion appliance with the highest particle emissions. Fine particle mass emission factors depend on many features including fuel characteristics and combustion conditions. Fireplaces operate with higher levels of excess air, which in turn is dictated by the uncontrolled amount of combustion air admitted to the reaction chamber.

Table 4.2 Fine particulate emission factors and chemical composition of selected Portuguese biomass fuel types.

Appliance	**Biomass type**	**$PM_{2.5}$ emission factor** ($g\ kg^{-1}$ fuel burned, dry basis)	**OC** (wt % of $PM_{2.5}$ mass)	**EC** (wt % of $PM_{2.5}$ mass)	**Water soluble ions** (wt % of $PM_{2.5}$ mass)	**Metals** (wt % of $PM_{2.5}$ mass)	**Σ of chemical components** (wt % of $PM_{2.5}$ mass)
Fireplace	Maritime pine	14.2	43.2	7.5	1.8	0.392	91.8
	Eucalypt	20.2	43.2	2.2	2.9	0.835	82.8
	Cork oak	13.4	51.8	2.6	0.64	0.510	98.5
	Golden wattle	10.0	38.7	6.6	11.3	2.48	84.6
	Olive	9.9	48.5	4.2	0.98	0.981	95.9
	Portuguese oak	19.1	48.0	2.5	1.87	1.27	92.2
	Holm oak	16.0	53.0	2.2	0.75	0.540	99.9
	Briquettes	15.3	47.7	5.4	2.7	0.596	96.4
Woodstove	Maritime pine	16.3	49.2	3.9	1.7	0.179	95.6
	Eucalypt	6.7	48.0	3.7	3.2	1.35	94.6
	Cork oak	15.1	53.6	1.9	0.53	0.394	100
	Golden wattle	11.7	45.0	2.0	13.6	1.97	87.6
	Olive	6.2	45.6	7.7	1.4	1.49	97.5
	Portuguese oak	9.8	49.4	3.9	1.6	1.26	97.3
	Holm oak	10.2	53.4	2.2	1.82	0.610	101
	Briquettes	4.2	47.1	3.9	9.1	2.17	94.7

Σ chemical components = $OC \times 1.8 + EC + NH_4^+ + Cl^- +$ Metals

When compared to woodstoves, this may cause dissimilar firebox conditions (biomass combustion rates, fuel chemistry, fuel physical properties, fuel geometry, temperatures, etc.) and, therefore, different emissions.

Assuming a heating value of 18 MJ kg^{-1} of dry biofuel (Telmo and Lousada, 2011), the particle mass emission factors (mg $PM_{2.5}$ MJ^{-1} biofuel) obtained in this study were compared with those of an Austrian energy-efficient "chimney type" stove burning typical Portuguese woods and other values from the literature (Table 4.3).

Table 4.3 Particle emission factors for different types of combustion appliances. Values are reported as mg particles emitted per MJ of fuel burnt.

		Type of combution appliance			
		Open fireplace	**Conventional woodstove**	**Modern woodstove**	**Chimney-type stove**
This study	$PM_{2.5}$	550 – 1122 (820)	233 – 906 (557)		
Karvosenoja et al. (2008)	$PM_{2.5}$	800	700		
Jokiniemi et al. (2008)	$PM_{2.5}$		100	34	
Sternhufvud et al. (2004)	$PM_{2.5}$		150 – 2100	330	
Pettersson et al. (2011)	PM_{tot}			38–350	
Gonçalves et al. (2010)	PM_{10}				70 – 183 (114)
Nussbaumer et al. (2008)	PM_{10}	860 – 910	50 – 1932		

Individual values are mean emission factors; ranges indicate minimum and maximum values; values in brackets are averages.

It should be noted that the Austrian wood heater emission limit has been set at 60 mg MJ^{-1}. The $PM_{2.5}$ emission factors for the fireplace and the woodstove are in the range of values reported for identical household combustion appliances in Scandinavia. However, particle emissions from the typical Portuguese woodstove are much higher than those obtained in the "chimney type" stove and in other modern combustion devices. Thus,

it seems that the major differences in emission factors are due to large variations in combustion technology.

For the same wood types, particle emissions from the traditional Portuguese stove were about 8-fold higher than those from the eco-labelled appliance (Table 4.4).

Table 4.4 Comparison between $PM_{2.5}$ emission factors and EC mass fractions from this study and those obtained for an eco-labelled "chimney type" stove burning the same Portuguese wood species.

EF $_{PM_{2.5}}$ (g kg^{-1}, dry basis)	**Gonçalves et al. (2010)**	**Present study Fireplace**	**Present study Woodstove**	**Ratio previous study/present study for stove**
Maritime pine	1.2	14.2	16.3	13.6
Eucalypt	2.1	20.2	6.7	3.2
Cork oak	2.9	13.4	15.1	5.2
Golden wattle	1.3	10.0	11.7	9.0
Average	1.9	14.4	12.4	7.7
% EC	**Gonçalves et al. (2010)**	**Present study Fireplace**	**Present study Woodstove**	**Ratio previous study/present study for stove**
Maritime pine	37.1	7.5	3.9	0.11
Eucalypt	13.4	2.2	3.7	0.28
Cork oak	11.3	2.6	1.9	0.17
Golden wattle	24.3	6.6	2.0	0.08
Average	21.5	4.7	2.9	0.16

In the fireplace and the old type stove, OC dominated the emissions, while more efficient combustion in the "chimney-type" stove contributed to 4 to 12-fold higher EC relative fractions in PM. In our experiments, the EC-to-total carbon (TC=OC+EC) ratios ranged globally from 0.03 to 0.15. An increase in the ratios with increasing combustion temperature was observed. Bølling et al. (2009) reported EC/TC ratios from 0.01 to 0.11 for low-temperature combustion in conventional stoves, confirming that PM from these combustion conditions are dominated by OC. Comparatively, EC/TC ratios for incomplete high-temperature combustion in stoves and masonry heaters have been reported to range from approximately 0.5 to 0.75 (Bølling et al., 2009). In the present study, OC contributed to approximately 50% of the fine particle mass in the emissions from every wood species studied, representing, on average, 92±4% of total carbon in $PM_{2.5}$. Lower percentages (58±15%) are characteristic of emissions from fossil fuel combustion in vehicles (Watson

et al., 2001). An average OC/EC ratio of 15.4±7.24 was obtained for the wood combustion experiments. Although coal, gas, and oil combustions may occasionally have comparable OC/EC emission ratios to biomass burning, in general, these emissions have low OC/EC ratios (Zeng and Wang, 2011). Ratios < 1 have been obtained at tunnel and roadside sites, where vehicle exhausts were identified as major sources of carbonaceous aerosols (Cheng et al., 2010). The OC/EC ratio from measurements in a busy roadway tunnel in central Lisbon was in the range of 0.3 to 0.4 (Pio et al., 2011).

A mass balance requires conversion from organic carbon mass to total organic compound mass using a factor that accounts for the hydrogen, oxygen, nitrogen, sulphur and other atoms content of the organic compounds present. In a review of biomass burning emissions with emphasis on forest fires, Reid et al. (2005) suggested an organic mass/organic carbon (OM/OC) ratio in the 1.4–1.8 range. Reff et al. (2007) reported values from 1.7 to 2.6 for urban residential outdoor aerosols. Alves et al. (2010) obtained an average ratio of 1.9 for $PM_{2.5}$ aerosols from prescribed fires in a Mediterranean shrubland. In this study, an OM/OC of 1.8 was adopted. Taking into account the gravimetric data and the mass of all quantified species, it is possible to make an attempt of reconstructing the $PM_{2.5}$ mass (Table 4.2). The resulting mass underbalances are most likely related to unaccounted chemical species or to the fact that a slightly higher OM/OC value should have been used.

The water-soluble ions accounted for about 1 to 14% of the $PM_{2.5}$ mass (Table 4.5). The golden wattle smoke presented a much higher ionic content, principally due to Cl^-, Na^+ and K^+, than the emissions from the burning of the other wood types. This high ionic content may be related to the characteristics of the ecosystem where the trees have grown. The golden wattle wood came from coastal dunes always subjected to saltwater spray from the Atlantic Ocean and, sporadically, to tidal flooding. *Acacia* species have been described as one of the salt-tolerant non-halophyte groups with the capability to regulate osmotically by utilising salts for preserving turgor and thus growth at high salinities (Ashraf et al., 2006). An excess of positive ions was observed, which could derive from the fact that not all the major anionic components were measured. It has been reported that biomass burning may contain significant amounts of water-soluble formate, acetate, oxalate and other organic anions, such as malonate, succinate and glutarate (Song et al., 2005).

Table 4.5 Water-soluble ions in the smoke samples. Values are given in µg mg^{-1} $PM_{2.5}$.

	Woodstove								Fireplace							
Ion	Pine	Golden wattle	Holm oak	Olive	Eucalypt	Cork oak	Portuguese oak	Briquettes	Pine	Golden wattle	Holm oak	Olive	Eucalypt	Cork oak	Portuguese oak	Briquettes
Na^+	ND	1.47	ND	ND	ND	ND	ND	ND	ND	1.82	ND	ND	ND	ND	ND	ND
NH_4^+	0.492	2.48	0.300	0.209	0.518	0.107	0.223	2.52	ND	1.29	0.154	0.141	0.447	0.242	0.229	0.736
K^+	0.150	13.0	5.50	7.14	8.73	4.23	9.89	13.3	2.30	11.0	4.65	4.83	9.04	3.99	11.5	2.56
Mg^{2+}	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.025	ND	ND	0.019	ND	ND	ND
Ca^{2+}	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cl^-	1.20	8.32	0.974	0.464	1.77	ND	0.368	5.21	1.52	7.07	0.128	1.507	0.355	ND	0.496	1.67
NO_3^-	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
SO_4^{2-}	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Detection limits (in µg g^{-1} $PM_{2.5}$): Na^+ - 0.087, NH_4^+ - 0.017, K^+ - 0.028, Mg^{2+} - 0.003, Ca^{2+} - 0.058, Cl^- - 0.046, NO_3^- - 0.290, SO_4^{2-} - 6.109

Table 4.6 Major trace elements present in the smoke samples. Values are given in µg g^{-1} $PM_{2.5}$.

		Woodstove								Fireplace							
Element	Symbol	Pine	Golden wattle	Holm oak	Olive	Eucalypt	Cork oak	Portuguese oak	Briquettes	Pine	Golden wattle	Holm oak	Olive	Eucalypt	Cork oak	Portuguese oak	Briquettes
Aluminum	Al	49.3	ND	65.4	1705	905	155	88.1	909	110	186	97.0	142	5.68	356	95.7	542
Barium	Ba	9.86	54.7	102	49.1	102	42.5	44.1	168	ND	ND	ND	13.2	ND	7.69	6.09	11.8
Calcium	Ca	82.2	ND	ND	ND	ND	ND	ND	ND	ND	774	ND	407	ND	48.1	43.5	62.3
Iron	Fe	440	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Lead	Pb	3.33	7.47	8.06	12.9	35.0	4.64	12.2	1361	2.89	30.3	2.97	8.04	0.319	8.70	7.88	616
Magnesium	Mg	37.0	ND	ND	ND	ND	ND	33.0	80.2	26.3	209	ND	61.0	1.38	28.8	34.8	68.5
Manganese	Mn	2.96	1.39	108	12.3	9.28	2.32	11.6	38.8	2.37	10.4	12.3	8.04	0.333	3.41	5.88	10.3
Nickel	Ni	0.534	ND	6.97	ND	ND	ND	ND	ND	1.47	ND	0.057	1.22	ND	0.961	0.087	0.436
Phosphorus	P	82.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	203	ND	96.1	74.0	187
Platinum	Pt	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Potassium	K	440	14123	5800	13107	12459	3739	12412	19171	2667	12593	5288	7294	9800	4406	12300	3904
Sodium	Na	617	5469	ND	ND	ND	ND	ND	ND	1052	7972	ND	203	ND	144	87.0	560
Strontium	Sr	0.411	1.82	2.83	2.17	3.25	1.06	2.75	8.56	0.053	7.82	ND	4.27	0.015	1.06	1.09	1.49
Titanium	Ti	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.464	ND	0.203	ND	ND	ND	0.560
Zinc	Zn	24.7	ND	ND	ND	ND	ND	ND	ND	57.9	ND	ND	ND	ND	ND	ND	ND

Detection limits (in µg g^{-1} $PM_{2.5}$): Al – 0.0202, Ba – 0.0002, Ca – 0.0806, Fe - 0.0012, Pb – 0.0002, Mg – 0.0121, Mn – 0.0002, Ni – 0.0002, P – 0.0121, Pt – 0.0002, K - 0.0403, Na – 0.0323, Sr – 0.0002, Ti – 0.003, Zn - 0.0028

The water-soluble potassium (K^+) comprised 77±20% and 71±30% of the analysed inorganic ions in particles emitted from the fireplace and the woodstove, respectively. A good correlation between the potassium levels determined by ICP-MS and the water-soluble form of the element was found ($K_{water\ soluble} = 0.73 \times K_{ICP\text{-}MS} + 0.06$; r^2=0.89). Thus, most of the potassium observed in the wood smoke emissions of this study is water-soluble, as indicated by the high K^+/K ratios: 0.80±0.19. Watson et al. (2001) reported K^+/K ratios ranging from 0.1 in geological material profiles to 0.9 in vegetative burning emissions. Previous studies also suggested that wood smoke potassium is water-soluble but that K in crustal particles is in a mineralised form (Calloway et al., 1989).

The elemental potassium, determined by ICP-MS, accounted for 0.87±0.52 wt % of $PM_{2.5}$, representing 0.092±0.058 g kg^{-1} wood burned. Fine et al. (2001) obtained an average potassium emission factor of 4.9±1.5 g kg^{-1} of wood burned, which corresponded to 1.1±0.4 wt % of fine particle mass from fireplace combustion of woods grown in the USA. Tissari et al. (2007) obtained potassium emission factors in the range 0.024–0.314 g kg^{-1} for the residential wood combustion in Finland using seven different appliances. Frey et al. (2009) determined K^+ emissions from a masonry heater of 0.29±0.03 g kg^{-1} wood burned in "normal" operation conditions, whereas a lower emission of 0.08 g kg^{-1} for the smouldering combustion phase was found. In addition to differences in wood types and burning appliances, one reason for variations in emissions may have to do with analytical methods. While Frey et al. (2009) analysed potassium as ionic compound, in the studies of Tissari et al. (2007) and Fine et al. (2001) potassium was determined as elemental component using ICP-MS and X-ray fluorescence, respectively. It should be also noted that potassium emission factors vary greatly depending on combustion conditions. Combustion of woody biomass in modern small scale units (modern log woodstoves with secondary air and automated air supply, and pellet stoves) provides favourable conditions with higher temperatures (>900ºC), good oxygen supply and sufficient mixing between combustible gases and air in the chamber (Boman et al., 2004). This result in almost complete combustion and the emissions are enriched in inorganic ash particles, such as alkali salts of potassium. Particles generated by low combustion temperatures (such as those observed in the two combustion appliances of this study) or incomplete combustion are characterised by a low content of inorganic constituents such as potassium, sulphur and chlorine (Bølling et al., 2009; and references therein).

In accordance with previous studies (e.g. Schauer et al., 2001), the potassium content of the fine particle emissions from pine wood was much lower than in the smoke of other species (Table 4.6). This difference may be important if potassium is used as a tracer for conifer and hardwood smoke particles.

Also like other biomass burning studies (Frey et al., 2009; McDonald et al., 2000; Schauer et al., 2001), Cl^- has also been identified as one of the main ions in emissions. The average emission factor for Cl^- found in our study was 207 mg kg^{-1} wood burned, reaching a maximum value of 969 mg kg^{-1} in the Golden wattle smoke. Schauer et al. (2001) obtained average chloride emission factors from fireplaces of 27.6, 10.2 and 144.5 mg kg^{-1} of pine, oak and eucalypts, respectively.

Particulate-phase nitrogen was essentially measured in the form of NH_4^+, accounting for a very small fraction of the $PM_{2.5}$ mass. The left over fuel nitrogen was likely emitted in the form of NO, N_2O, N_2, HCN, and nitrogen-containing organic species or remained in the bottom ash following the burn (McMeeking et al., 2009). The ratio of the concentration of NH_4^+ to the sum of the concentration of SO_4^{2-} and NO_3^- (in neq/neq) is used to assess the acidity of aerosols. Neutralisation ratios of unity suggest the presence of sulphate and nitrate as their ammonium salts. Ratios < 1 imply the likely presence of acidic aerosols, while values > 1 probably arise from the presence of NH_4Cl (Balasubramanian et al., 2003). Concentrations of SO_4^{2-} and NO_3^- in the smoke particles above the detection limit contribute to very high neutralisation, suggesting the dominance of NH_4Cl. In other biomass burning experiments, KCl and NH_4Cl have been found in smoke, dominating the ionic fine particles as condensation products (e.g. Andreae et al., 1998; Liu et al., 2000).

Equilibrium calculations and the chemical characterisation of smoke particles in previous works (e.g. Sippula et al., 2007) revealed that homogeneous nucleation or heterogeneous condensation of alkali metals, such as Na and K, upon existing seed particles depend on temperature. While at lower temperatures (<550ºC), such as those observed in domestic fireplaces and woodstoves, the alkali metals condense as chlorides or hydroxides, the occurrence of sulphation reaction and formation of alkali sulphates, such as K_2SO_4, only take place at temperatures > 900ºC. These temperature-dependent mechanisms may explain the observation, in our study, of SO_4^{2-} levels below the detection limit. Another reason may be related to the low sulphur content of wood (Table 4.1).

Altogether the trace elements obtained by ICP-MS comprised 0.4 to 2.5% of the total fine particle mass with a global emission of 110±64 mg kg^{-1} wood burned. Among these, K, Pb, Al, Mn and Sr were present in all samples, contributing to more than 90% of the total ICP-MS mass. Other elements detected in emissions, but not always present, were Ba, Ca, Mg, Ni, P, and Na. The remaining trace elements analysed by ICP-MS were below the detection limit in any sample. The total trace element content in emissions from burning pine, Golden wattle, Holm oak, and cork oak in the fireplace was higher than the corresponding emissions from the woodstove. Burning eucalypts, olive, Portuguese oak or briquettes in the woodstove contributed to fine particle emissions with a higher metal content compared to that in the fireplace smoke. Emission factors for the main elements are given in Table 4.6. Since trees absorb these elements from water and soil, and taking into account that the availability of trace metals in soils can differ from region to region, then a lack of correlation among wood burning emission profiles in the literature is likely to exist (Gonçalves et al., 2010; Schauer et al., 2001; Schmidl et al., 2008; Tissari et al., 2007). Among heavy metals, lead is a potential pollutant that readily accumulates in soils. Although lead is not an essential element for plants, it gets easily absorbed and accumulated in different plant parts. Uptake of Pb in plants is regulated by pH, particle size and cation exchange capacity of the soils as well as by root exudation and other physico-chemical parameters (Sharma and Dubey, 2005). Aluminium is not regarded as an essential nutrient, but low concentrations can sometimes increase plant growth or induce other desirable effects. Al is present in all soils, but Al toxicity is manifested only in acid conditions, in which the phytotoxic form Al^{3+} predominates (Rout et al., 2001). Manganese is one of the microelements, which are actively adsorbed by vegetation and have a major effect on the formation of plant mass. Mn is involved in a number of physiological processes. It is important for the synthesis of the organic substances and the metabolism of nutrient elements (e.g. Ca^{2+} and Mg^{2+}) in plants (Beck et al., 2006). Due to the physico-chemical similarities of strontium (Sr^{2+}) to calcium (Ca^{2+}), both elements can easily be taken up by plants. In addition to the apoplastic pathway into the xylem, different Ca^{2+} channels are associated with Sr^{2+} accumulation (Kanter et al., 2010). Biomass burning may result in the volatilisation of these trace metals which then undergo condensation or gas-to-particle type reactions, adsorbing on the surface of pre-existing aerosols.

Barium was an element always present in the $PM_{2.5}$ emissions from the woodstove. Its absence from the fireplace smoke suggests that the emission likely depend on combustion conditions. It is possible that some Ba is held organically and is released from the parent fuel as single barium atoms during burnout of the organic matrix (Miller et al., 2006). The higher temperatures registered in the woodstove burning chamber compared to those in the fireplace may have led to the rapid release of barium as its organic host was consumed. Barium was also detected as one of the most abundant metals in the smoke from wildfires in Portugal (Alves et al., 2011). The element is naturally present in soils at relatively high concentrations. Plants growing on Ba-rich soils usually contain high Ba concentrations, although considerable differences between species have been reported (Suwa et al., 2008). Schmidl et al. (2008) also found barium in emissions from woodstove combustion of common woods growing in mid-European Alpine regions, at levels ranging from 0.0026 to 0.0047 wt % of $PM_{2.5}$ mass.

In our study, P varied from levels below the detection limit to 2.84 mg kg^{-1} wood (briquettes), while Schauer et al. (2001) reported emissions ranging from 0.38 mg kg^{-1} wood (pine) to 1.02 mg kg^{-1} wood (eucalypts). Ni, an essential element for plant metabolism (Chen et al., 2009), was found in the smoke of pine, Holm oak, olive, cork oak and briquettes with emission factors up to 0.02 mg kg^{-1} wood, while Schauer et al. (2001) did not detect the element at quantifiable levels. However, Ni was always present in the smoke emissions from woodstove combustion of common Austrian woods (Schmidl et al., 2008).

4.3.2 Cluster analysis

A cluster analysis using WinSTAT, the statistical add-in for Microsoft® Excel, was done to exploit differences and similarities in the composition of individual wood combustion profiles obtained for OC, EC and the major inorganic species. The cluster dendogram in Figure 4.1 shows that emissions from burning olive in the fireplace or in the woodstove were separated into different clusters. The cork and Holm oak emissions, whether from the fireplace or from the woodstove, were grouped into the same cluster. Emissions from the combustion of eucalypts in both combustion appliances showed similarities with those from the Portuguese oak, since their emission data were branched together. Thus, while cork and Holm oak emissions may be averaged to obtain a single

composite emission profile, the Portuguese oak composition should not be used in the same pooling of data. The dissimilarities in the composition of the Golden wattle smoke resulting from the combustion in the fireplace or in the woodstove were separated and assigned to different branches.

In order to explain which chemical species are causing the formation of the two main clusters, another hierarchical cluster analysis focusing on the variables, by transposing the data matrix, was done. Two main clusters were distinguished on the dendrogram obtained (not shown): the first includes OC, the second assembles the inorganic variables and EC. Identical result was obtained after application of a standardisation procedure to each input variable by subtracting its mean and dividing by its standard deviation.

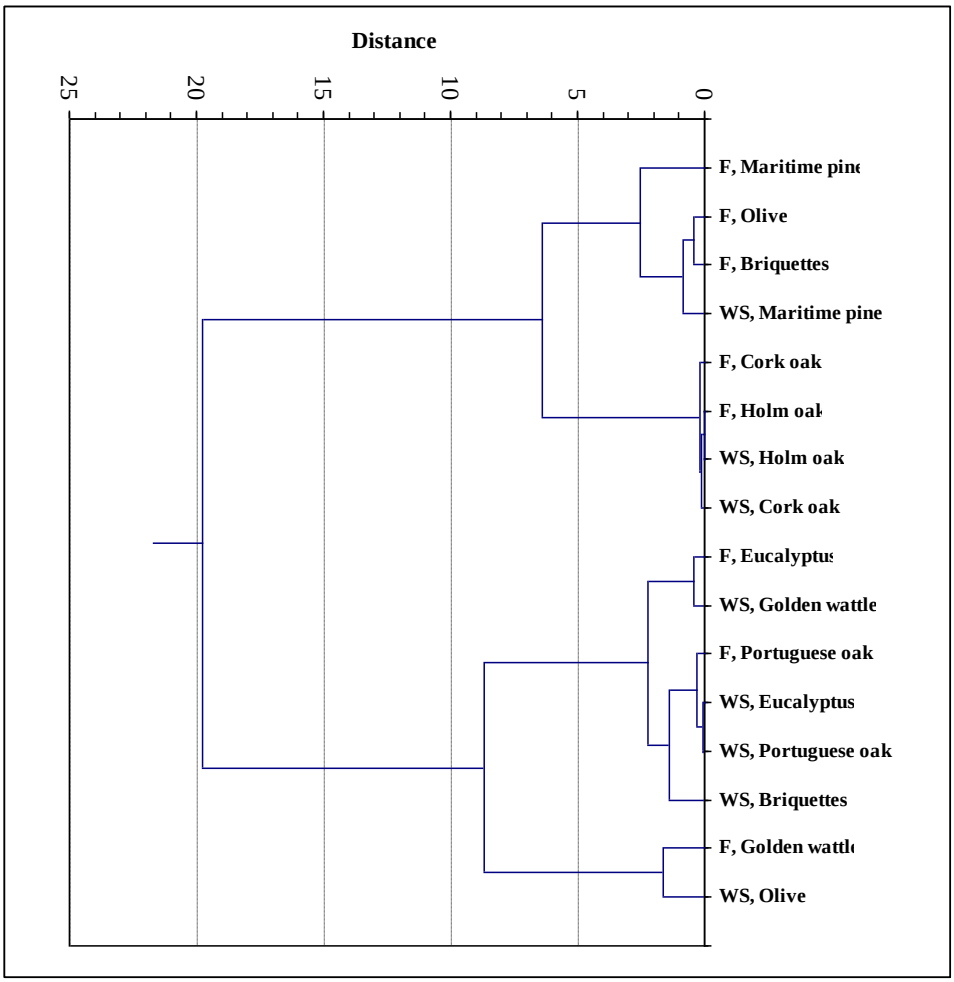

Figure 4.1 Hierarchical clustering (Ward's method) of wood combustion source samples (F – fireplace, WS – woodstove).

4.4 Conclusions

This paper reports a comprehensive effort to characterise particle emissions from residential wood combustion. The heating appliances used (fireplace versus stove) and the type of biomass fuel (hardwood, softwood, and manufactured fuel) had the largest effect on the emission characteristics. On average, the $PM_{2.5}$ emissions were higher for the fireplace than for the woodstove. More than 80% of the mass of the smoke particles were composed of organic matter, while water-soluble ions and trace elements represented a small fraction, with variable contributions, depending on the burning experiment. This overwhelming proportion of carbonaceous constituents in smoke particles from the low-temperature combustion equipments of this study differs from the fly ash composition of modern appliances with improved combustion conditions, good burn out and low emissions of PM, in which inorganic salts dominate.

From the 67 elements that have been searched for, 20 were typically found at quantifiable levels, but only K, Pb, Al, Mn and Sr were always detectable in the smoke from all wood types. Among these, potassium presented the highest concentrations. High K^+/K ratios, similar to those reported in the literature for vegetative burning emissions, point out that most of the potassium is water-soluble. The application of cluster analysis to the individual smoke composition indicated that emissions from the cork and Holm oak combustion, whether in the fireplace or in the woodstove, can be grouped into the same composite source profile, while those from the Portuguese oak should be separated into another profile, which also may include the emissions from eucalypts. Emissions from the combustion of maritime pine in both appliances may also be averaged to obtain a single profile.

The comparison of emissions from this study with literature data showed significant differences between the various types of combustion equipments, especially old-type residential appliances versus modern woodstoves and boilers with higher combustion efficiency. More detailed characterisation of the variations in particle properties between the different types of appliances is however still wanted, taking into account the vast array of technologies and models. To appropriately use emission profiles for biomass burning in source attribution studies, it is also desirable to extend the residential combustion experiments to further trees growing in forests and gardens from other Mediterranean countries.

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CHAPTER 5

Chapter 5. Organic particulate emissions from field burning of garden and agriculture residues

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Abstract

To assess the particulate matter (PM) composition, the smoke from three different agriculture and garden residues, commonly subjected to open field burning in Northern Portugal (potato haulm (A), arable weed vegetation (B) and collard greens stalks/pruned green leafy-twigs (C)) have been sampled into 3 different size fractions ($PM_{2.5}$, $PM_{2.5-10}$ and $PM_{>10}$). To replicate another frequent practice of reducing or dispose agriculture/garden debris, residue C was complementarily burned in a metal container with addition of used lubricant oil. The size-segregated aerosol samples were analysed for elemental (EC) and organic (OC) carbon by a thermal-optical transmission technique. The organosoluble OC was fractionated by vacuum flash chromatography and analysed by gas chromatography-mass spectrometry (GC-MS). Burning of residue C produced the highest PM emissions. OC was the dominant carbonaceous component in all aerosol samples, contributing to about 98% of total carbon (TC). The detailed chemical profiles of particulate emissions, including organic tracer compounds, have been assessed. The contribution of phenolics (0.2–39% OC, w/w) and organic acids (1.5–13% OC, w/w) to OC was always predominant over other organic compounds, whose distribution patterns were found to vary from one residue to another. The polyphenols, as the guaiacyl derivatives, were particularly abundant in PM from the residue C burning, but anthropogenic constituents completely superimposed the emission profiles after addition of used lubricant oil. It was shown that the prevailing ambient conditions (such as high

humidity) likely contributed to atmospheric processes (e.g. coagulation and hygroscopic growth), which influenced the particle size characteristics of the smoke tracers, shifting their distribution to larger diameters. Since it was shown that the relative contribution of different carbon forms and organic compounds may strongly depend on the size of the particulate matter, the barely analysis of one size fraction cannot be reliable enough to assess neither global emission tendencies nor the profiles of individual chemical components in smoke.

Keywords: Agriculture wastes, biomass combustion, PM, OC/EC, organic speciation.

5.1 Introduction

Open burning of agriculture and garden residues is a rapid method to reduce/dispose of vegetative debris and allows clearing of land and releasing of nutrients for the next growing cycle, fertilising the soil, and eliminating pests and weeds. As wildfires, agricultural burning is also an important source of toxic air pollutants into the atmosphere with instantaneous and short/long-term effects on human health (Jacobs et al., 1997; Long et al. 1998; Tirigoe et al., 2000), significant impact on air quality (Chen at al., 2008; Fang et. al., 1999; Li et al., 2010; Ortiz de Zárate et al., 2005; Ryu et al., 2007; Ulevicius et al., 2010; Yang et al., 2008) and global climate change (Christopher et al., 1998; Levine at al., 1995;). Carbon dioxide (CO_2), carbon monoxide (CO), particulate matter (PM) and non methane hydrocarbons (NMHC) are major components of agricultural burning smoke. On a global scale, the estimated annual total dry matter combusted due to agricultural burning is around 540 Tg yr^{-1}, and the corresponding emissions are of 818 Tg CO_2 yr^{-1}, 50 Tg CO yr^{-1}, 1.3 Tg NO_x yr^{-1}, 3.5 Tg NMCH yr^{-1} and total particulate matter 7.0 Tg TPM yr^{-1}(Andreae and Merlet, 2001). These estimates and the impact of emissions on the atmosphere are somewhat uncertain, because consistent data on agricultural burning are much sparser than data on other anthropogenic sources.

PM resulting from burning of crop residues includes a large carbonaceous fraction (Liousse et al., 1996; Turn et al., 1997) with significant climate impacts. OC has the potential to scatter light directly and cools the atmosphere (Ramanathan et al., 2001) while EC absorbs solar radiation and heat the atmosphere (Liousse et al., 1996; Menon et al., 2002; Ramanathan and Carmichael, 2008).

Emissions from agricultural residue burning strongly depend on several factors, such as biofuel type, moisture content, meteorological conditions, burning techniques and how the refuse is arranged (in piles, rows, or spread out) (Oanh et al., 2011). In Portugal, agricultural burning is allowed between October 15 and May 15. Taking into account that agricultural burning in Southern Europe is in general carried out in spring and autumn, under moderate to high atmospheric humidity conditions (to reduce risks of uncontrolled fires), it is expected that emissions will be significantly different from those of wildfires. Also, the successive addition of small amounts of biomass to the combustion pile, during the burning process, renders agricultural burning a specific case with its own emission

profiles. The emission information for agricultural activities has been reported in some studies. Cao et al. (2008) and Li et al. (2007) reported PM emission factors, EC, OC, gaseous species (e.g. SO_2, NO_x, CO, and CO_2) and ionic constituents for the domestic burning of four types of commonly produced crop residues in rural China: rice straw, wheat straw, corn stover and cotton stalk. The PM size distributions and particulate emission factors (EF) of polycyclic aromatic hydrocarbon (PAHs) from burning in a combustion chamber of two common agricultural waste residues (biofuels) in California, almond prunings and rice straw, were studied by Keshtkar and Ashbaugh (2007). Dhammapala et al. (2007) investigated the burning of wheat and Kentucky bluegrass stubble in USA and determined the EF for OC, EC, PAHs, methoxyphenols and levoglucosan. The carbonaceous fractions, trace inorganic element composition, and methoxyphenols and levoglucosan emission ratios for the combustion of the same type of residues have been reported by Jimenez et al. (2007). Hui et al. (2007) characterised the aliphatic hydrocarbons and PAHs from the burning of two typical Malaysian garden wastes: bachang litter falls and grass. The detailed chemical characterisation of PM in smoke from burning rice straw, grasses, leaves and cereal straw has been reported by Hays et al. (2005), Oros et al. (2006), Schmidl et al. (2008) and Zang et al. (2007). Results from previous studies showed that burnings of agricultural residues can be a very significant source of pollutants, which may influence the air quality (Cheng et al., 2009; Jimenez et al., 2006; Li et al., 2010; Viana et al., 2008; Yang et al., 2006, Yang et al., 2008).

Despite previous research efforts have been done to obtain some emission profiles for the combustion of crop residues, the database covering the emissions from agricultural burning is limited, especially in Mediterranean regions. The main objective of this work is to provide the detailed chemical characterisation of $PM_{2.5}$, $PM_{2.5-10}$, and $PM_{>10}$ in smoke emissions from burning of different types of agricultural/garden residues and practices. Although not allowed in many European countries, open-air combustion of garden wastes, weeds, agricultural and pruning debris, vegetation from clearings, leaves, etc., is very widespread in Southern Europe countries, and particularly in Portugal.

5.2 Experimental

Three types of agricultural and garden residues (Table 5.1) produced by a farmer from the region of Aveiro, Portugal, were openly burned by the farmer in September 2009

under foggy conditions (near 100% atmospheric relative humidity). The first residue (sample A) included dried potato branches and leaves (haulm), the second (sample B) contained arable weed vegetation from multiple species and the third (sample C) comprised stalks from collard greens and pruned green leafy-twigs together with thin branches from garden trees. This third residue was additionally burned in a metal container where a small amount of used lubricant oil has been added to facilitate combustion (sample D). In spite of not being allowed, this practice is very common in the region.

Table 5.1 Type of agriculture/garden residues burned.

Sample	Type of residues
A	Potato (*Solanum tuberosum*) dry branches and foliage
B	Arable weed vegetation, including oat (*Avena sp*.), docks (*Rumex sp*.), bird's-foot (*Ornithopus perpusillus*), lamb's-quarters (Chenopodium album L.), black nightshade (*Solanum nigrum*), everlasting cudweed (*Gnaphalium luteo-album* L.), salvation jane (*Echium plantagineum* L.), redroot pigweed (Amaranthus retroflexus L.), common catchfly (*Silene gallica* L.), common ramping-fumitory (*Fumaria muralis*), red clover (*Trifolium pratense*), yellow clover (*Trifolium campestre*), scarlet pimpernel (*Anagallis arvensis* L.), chamomile (*Chamaemelum nobile* L.), spotted ladysthumb (*Polygorum persicaria* L.), and other less abundant *Gramineae* species
C	Stalks of collard greens (*Brassica oleaceata*, Acephala group), and pruned green leafy-twigs of bay laurel (*Laurus nobilis*), bougainvillea (*Bougainvillea spectabilis*) and avocado (*Persea americana)*
D	The same residues as those defined for sample C were burned in a 200 L metal container with multiple hollows close the bottom of the cylindrical body. To replicate a common agricultural practice, approximately 2 L of used lubricant oil were added to the container.

A schematic diagram of the open burning experiment is presented in Figure 5.1. A tripod high-volume sampler/impactor (Tisch Environmental Inc.) operating at a flow of 1.13 m^3 min^{-1} was used to collect sequentially, on pre-baked quartz fibre filters, coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$) smoke particles. The impaction system for capturing $PM_{>10}$ was designed at the University of Aveiro in accordance with the Marple and Rubow (1986). A Tisch impaction plate TE-231 F was used to separate particles at 2.5 µm. Quartz filters used as impaction substrates have been shown to minimise particle bounce without affecting the cutpoint of the impactor (Chang et al., 2001), and do have the advantage that they can be baked at 500°C prior use, which is necessary for measurements of the organic

fraction to avoid high blank values. On the other hand, when the amount of carbon is to be measured, sampling will have to be carried out on quartz filters because of their resistance to the heating process.

The sampler was positioned at about 2 m above ground to collect samples in the middle of the smoke column. The maximum distance to the combustion pile was around 8 m. In parallel and simultaneously, Tedlar bags previously flushed with N_2 have been used for the collection of gas samples. Pre-removal of water vapour from the air stream was carried out in a U glass tube filled with glass spheres, immersed in an ice bath. In addition, and previously to the water vapour removal, the air stream was filtered through a 4.7 mm quartz filter to remove particles before passing to the collection system, which also contained a Teflon-lined diaphragm pump connected to a needle valve and a calibrated rotameter operating at a flow rate of 1 L min^{-1}. Taking into account that these experiments do not represent simulated burnings and that it was decided not to interfere with the farmer's activities in order to have authentic fires, replicate burns were not performed. However, to obtain "average" emission factors or emission profiles for organic compounds, plume sampling was carried out from the ignition of each fire to the end of the smouldering phase. Each burning lasted between 30 and 60 min. The plume temperature at the sampling point was 20–25º C. One of the Tedlar bags was sampled in the same location prior to the burnings aiming to obtain background levels, which were afterwards subtracted from the smoke measurements. After sampling, the bags were stored in opaque containers in order to minimise U.V. radiation of the samples. The time period between sampling and analysis was reduced to a few hours to avoid secondary reactions.

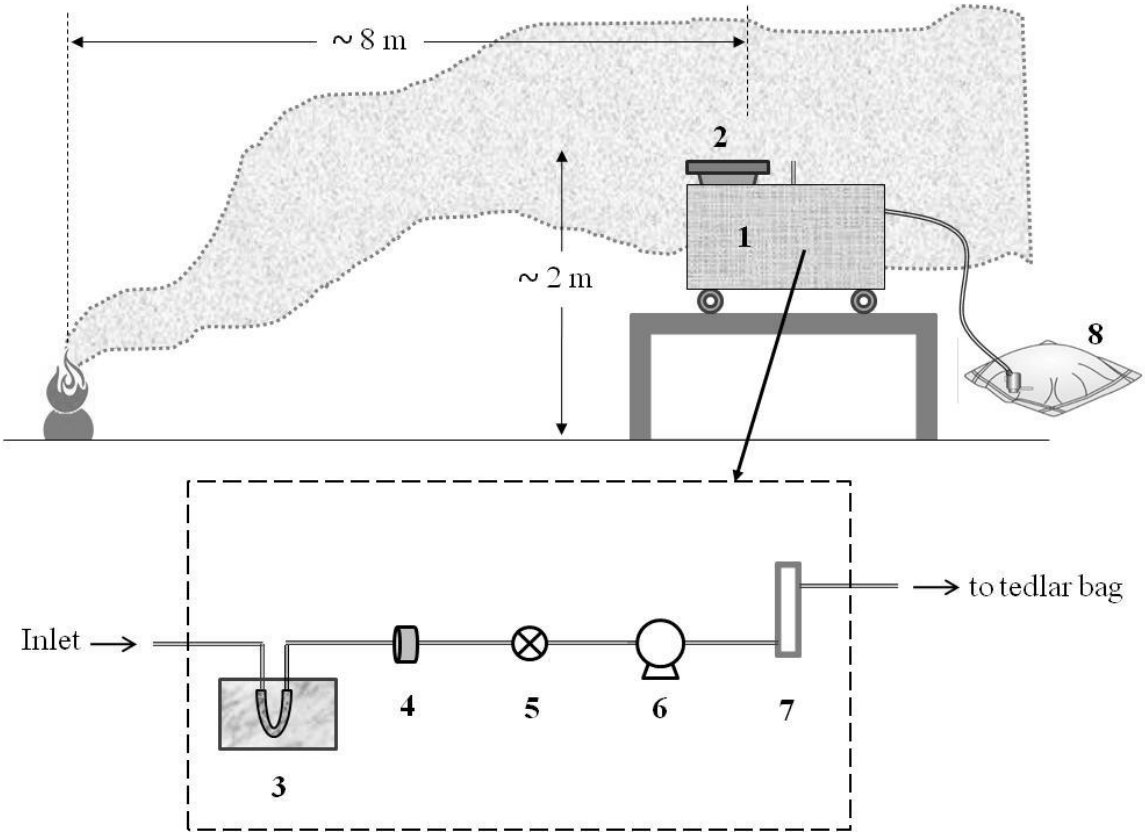

Figure 5.1 Schematic diagram of the experimental setup.

1) Portable box, 2) PM sampler, 3) U-shaped tube filled with small glass balls in an ice bath to remove water vapour, 4) Filter holder (Ø= 47 mm) to remove particles from the air stream, 5) Needle valve, 6) Teflon pump, 7) Rotameter, 8) Tedlar bag.

The gas phase samples were examined for CO_2 and CO using an infra-red analyser (Environnment, MIR 9000). It should be noted that the average modified combustion efficiency (MCE = $\Delta CO_2/(\Delta CO_2 + \Delta CO)$) calculated in relation to background levels was 0.88 ± 0.02. This indicates a mixture of smouldering and flaming combustion for all the open burning experiments. Pure smouldering usually has MCE below 0.85 (Yokelson et al., 1997). The flaming combustion usually exhibits the highest MCE values (0.9-1) (Reid et al., 2005).

The carbonaceous content (EC and OC) of particulate matter was analysed in filter punches by a thermal–optical transmission technique following a short multi-step temperature protocol, first in an inert (N_2) and then in an oxidising atmosphere (N_2/O_2) (Alves et al., 2010b). Another parts of the filters (80% and 9% of total area for $PM_{>10}/PM_{10}$ and $PM_{2.5}$, respectively) were extracted with dichloromethane and separated into different

organic fractions by flash chromatography using various solvents of increasing polarity. To test the recoveries, blank filters previously spiked with known quantities (five different concentration ranges) of representative organic standards were extracted and analysed. For the whole procedure of extraction and analysis, reproducible results of 75±12% and 95±8% were, respectively, obtained for polar and non-polar compounds. In the case of levoglucosan (the main anhydrosugar from biomass burning), the extraction and fractionation procedure enabled a recovery of 70±5%. The fractionated extracts were analysed by gas chromatography-mass spectrometry (GC-MS model 9890, quadrupole 5973 GC from Hewlett-Packard and, GC Trace Ultra, quadrupole DSQ II from Thermo Scientific) after application of appropriate derivatisation techniques to the more polar organic fractions. The GC-MS system was accurately calibrated using about 150 high purity individual compounds at five different concentration levels. All samples and authentic standards were injected with two internal standards: tetracosane-d50 (Sigma-Aldrich) and 1-chlocohexadecane (Merck). Additionally, the EPA 8270 semi-volatile internal standard mix (Supelco), containing six deuterated compounds (1,4-dichlorobenzene-d4, naphthalene-d8, phenanthreme-d10, chrysene-d12, perylene-d12), has been used for PAHs analysis. The overall inaccuracy of the calibration procedure did not exceed 10% for the aliphatic fraction, 12% for polycyclic aromatic compounds, 13% for carbonyl compounds, 6% for *n*-alkanols and sterol compounds, 3% for acids and 11% for sugars. The methodology for the extraction, flash chromatography and GC-MS analysis was previously described in detail by Alves et al. (2010b).

An emission factor is defined as the amount of any compound released per amount of dry fuel burned and expressed in g kg^{-1}. The emission factor of a species *n* (EFn) can be obtained from the ratio between the mass concentrations of this species and the carbon emitted in the plume (Alves et al., 2011). To convert to grammes of species *n* emitted per kg of dry mass burned, this ratio was multiplied by the mass fraction of carbon in the dried fuel, which was taken as 48% (Silva et al., 2008):

$$EF_n = \frac{[\ ]}{[CO_2] + [CO] + [\text{Hydrocarbons}] + [TC]} \times \%C_{fuel}$$

The carbon released was estimated as a sum of concentrations of CO, CO_2, hydrocarbons and total particulate carbon (TC = OC + EC). The hydrocarbon concentrations were not measured and, consequently, not accounted for in the calculation of the carbon emitted. However, it has been estimated that hydrocarbons represent only around 3% of the carbon emitted from several wildfires in Portugal (Alves et al., 2011) and shrubland burnings (Alves et al., 2010a). Thus, the emission factors calculated in this work correspond to upper limits of the real values.

5.3 Results and discussion

5.3.1 Emission factors and carbonaceous content of PM

Concentrations for PM, and the OC, EC and TC components of the smoke aerosol are summarised in Table 5.2. The concentrations of $PM_{2.5}$, $PM_{2.5-10}$ and $PM_{>10}$ in smoke from samples A and B showed values of the same order, in the ranges of 1197-2239, 462-578 and 7135-8348 μg m^{-3}, respectively. However, the $PM_{>10}$ concentrations for samples C and D were twice higher, achieving values of 16906 and 18555 μg m^{-3}, respectively. The $PM_{2.5-10}$ concentrations were around 6-fold higher for the open burning of sample C compared to the burning of the same residues in the container with used lubricant oil (sample D). The $PM_{>10}$ concentrations were significantly higher when compared to fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) fractions for all samples. These results diverge from those presented in many studies, which suggested that biomass burning mostly produces sub-micrometer particles (Chen et al., 2010; Levin et al., 2010; Reid et al., 2005). The particle size distributions of smoke aerosols depend on several factors, including the inherent properties of the biofuel, the specific burning method and combustion parameters, environmental factors, as well as atmospheric processes, such as coagulation, hygroscopic growth, and resuspension of soil and ashes (Carrico et al., 2010; Engling et al., 2009). It was shown by Kleeman et al. (2008) in laboratory combustion tests that fresh rice straw smoke particles have a distinct shift to larger particle sizes compared to other types of biomass, such as oak wood. It has also been observed that the slow burning process of agricultural residues that is in close contact with the underlying top soil is characterised by low combustion efficiency, producing larger smoke particles compared to faster burning (Wardoyo et al., 2007).

Table 5.2 Emission factors, particulate matter concentrations and carbonaceous fractions in the smoke from the agriculture/garden residue burning.

	Potatoes			Arable weed vegetation			Stalks of collard greens, etc.			Container		
	$PM_{2.5}$	$PM_{2.5-10}$	$PM_{>10}$	$PM_{2.5}$	$PM_{2.5-10}$	$PM_{>10}$	$PM_{2.5}$	$PM_{2.5-10}$	$PM_{>10}$	$PM_{2.5}$	$PM_{2.5-10}$	$PM_{>10}$
PM[a] (this study)	2239	462	7135	1197	578	8348	1378	4608	16906	1204	772	18555
OC[b] (this study)	4.65	15.5	60.6	7.92	23.9	54.1	18.5	59.2	32.3	14.9	15.1	75.8
EC[b] (this study)	0.89	< LD[d]	0.75	< LD	< LD	1.06	< LD	0.65	0.60	< LD	< LD	0.86
TC[b] (this study)	5.54	15.5	61.3	7.92	23.9	55.2	18.5	59.9	32.9	14.9	15.1	76.7
OC/EC (this study)	5.20		81.3			51.3		91.2	53.6			87.9
TC/PM[c] (this study)	5.54	15.5	61.3	7.92	23.9	55.2	18.5	59.9	32.9	14.9	15.1	76.7
EF_{PM}[e] (this study)	6.47	1.34	20.1	0.90	0.43	6.22	1.34	4.45	16.2	0.93	0.59	14.0
EF_{CO}[e] (this study)		106			116			147			141	
EF_{CO2}[e] (this study)		1547			1564			1499			1499	
EF_{OC}[e] (this study)	0.30	0.21	12.2	0.07	0.10	3.37	0.25	2.63	5.24	0.14	0.09	10.6
EF_{EC}[e] (this study)	0.06		0.15			0.07			0.10			0.12
Rice straw (Oanh et al., 2010)	$EF_{PM2.5}$[e] = 8.3 ± 2.7; EF_{PM10}[e] = 9.4 ± 3.5											
Foliar Fuels (Hays et al., 2002)	$EF_{PM2.5}$[e] = 11.2 – 33.5; EF_{OC}[e] = 8.0 – 27.8; EF_{EC}[e] = 0.2 – 1.3											
Wheat/Rice straw (Hays et al., 2005)	$EF_{PM2.5}$[e] = 4.71 ± 0.04/12.95 ± 0.30; EF_{OC}[e] = 1.23 ± 0.03/8.94 ± 0.42; EF_{EC}[e] = 0.52 ± 0.00/0.17 ± 0.04											
Wheat/Kentucky bluegrass stubble (Jimenez et al., 2007)	$EF_{PM2.5}$[e] = 8.3 ± 4.4/22.4 ± 0.2											
Wildland fuels (Chen et al., 2007)	$EF_{PM2.5}$= 2.2 – 10.3; EF_{CO2}[e] = 1456.4 – 1765.5; EF_{CO}[e] = 17.0 – 49.0											
Portuguese wood (Gonçalves et al., 2010)	EF_{PM10}[e] = 1.12 – 2.89											
Wildfires in Portugal (Alves et al., 2010c)	$EF_{PM2.5}$[e] = 19.3 ± 15.1; EF_{CO}[e] = 231 ± 117; EF_{CO2}[e] = 1000 ± 1700											
Mediterranean shrubland (Alves et al., 2010b)	$EF_{PM2.5}$[e] ≈ 3.8; EF_{CO2}[e] = 1615 – 1750; EF_{CO}[e] = 0.2 – 78											

[a] mg m^{-3}; [b] %w/w PM; [c] %; [d] LD – Detection Limit (LD = 0.23 μg); [e] EF – Emission Factors (g kg^{-1} fuel burned, dry basis)

Although the hygroscopicity of biomass burning aerosols was found to be rather small in various ambient and laboratory investigations (Carrico et al., 2010; Svenningsson et al., 2006), a recent study of the hygroscopic growth of fresh smoke particles emitted from rice straw burning showed an unusually high particle growth factor of 1.5 at a relative humidity of 85% (Engling et al., 2009). Thus, due to the dense fog, the smoke aerosols generated in our study likely took up significant amounts of water forming larger particles.

The carbonaceous fraction of the aerosols was dominated by OC (OC/TC~98%). The OC/TC ratios reported in the literature are highly variable, given the sensitivity of OC emission to combustion conditions (e.g. combustion efficiency) and biofuel types (McMeeking et al., 2009). Similarly to our work, high OC/TC ratios (94-99%) were obtained for the burning of garden leaves and foliar fuels (Hays et al., 2002; Schmidl et al., 2008). However, larger variations in this ratio (70-98%) were reported for rice and wheat straw burning (Hays et al., 2005). The very high OC/TC ratios obtained in our study may result from condensation of large hydrocarbons, enhanced isoprenoid emissions, acid-catalysed reactions and rapid oxidation of low-volatility organic vapours (Grieshop et al., 2009; and references therein). It should be also noted that emissions resulting from low combustion efficiency processes (in this case, associated with the specific foggy condition and the contact with the underlying top soil) are very enriched in OC. Elemental carbon particles are typically emitted during the flaming stage.

The OC fractions in $PM_{2.5}$ (4.65–18.5%) were low compared with reported values (e.g., Carrico et al., 2010; Chow et al., 2004). Biomass fuel characteristics, as well the combustion conditions, exert a strong influence on the smoke aerosol composition and properties, including hygroscopicity. The presence of inorganic salts in the fuel matrix and their emission upon burning may model the inorganic-to-organic composition ratio of smoke, and consequently, the hygroscopic properties and the aerosol size distribution (Carrico et al., 2010; Lee et al., 2008). The chemical composition of the biofuels depends not only on the natural adaptations of plant species to environmental conditions, but also on the application of fertilisers or other products, in the case of crops. Thus, it is possible that agricultural/garden residues possess a higher inorganic content than other biofuels. On the other hand, it should be noted that the carbonaceous content obtained from the thermal-optical technique does not account for associated O, H, N, and other elements, from the measured C mass concentrations attributed to OC. To estimate the organic matter content

in particulate matter, the OC measurements have to be multiplied by a factor that could be higher than 2 (Alves et al., 2010a).

The OC/EC ratios in $PM_{>10}$ were rather high and similar for samples B and C (51 and 53, respectively). Moreover, the OC/EC ratios in $PM_{>10}$ of samples A and D were even higher (81 and 88, respectively). Very high OC/EC ratios (88 ± 46 for $PM_{2.5}$, 128 ± 73 for $PM_{2.5-10}$ and 93 ± 23 for $PM_{>10}$) were also previously reported for the smoke from prescribed burnings of a shrub-dominated forest with some pine trees (Alves et al., 2010a). OC/EC ratios published in other biomass burning works were lower than in the present study: 19–44 for grass smoke (Oros et al., 2006), 3–78 for conifer smoke (Oros and Simoneit, 2001a) and 9–43 for deciduous tree smoke (Oros and Simoneit, 2001b). However, these comparisons should be made with caution because application of distinct measurement techniques leads to different values (Watson et al., 2005). Results from interlaboratory comparison studies involving seventeen laboratories using nine different thermal and optical methods, positioned the University of Aveiro within the group with "best estimates" (Schmid et al., 2001). Furthermore, the comparison between the methodology of the University of Aveiro and the "European Supersites for Atmospheric Aerosol Research" (EUSAAR-2) protocol (Cavalli et al., 2009) for the quantification of the different carbon fractions in atmospheric aerosol samples produced similar results for OC and EC, without significant differences at a 95% confidence level (Nunes et al., 2010). It should be noted, however, that all the OC/EC ratios obtained in biomass burning experiments are substantially higher than those reported for other sources, such as coal burning (OC/EC=2.7) and motor vehicle exhaust (OC/EC=1.1) (Watson et al., 2001), and thus may be used as an indicative tool for source apportionment purposes.

EFs of $PM_{2.5}$ ($EF_{PM2.5}$) and PM_{10} (EF_{PM10}) obtained in this work were compared to those previously reported for burning of other agricultural residues (Table 5.2). $EF_{PM2.5}$ obtained for samples B, C and D were remarkably lower than EFs published for the main groups of agricultural/garden wastes. The only exception is sample A, which showed values of the same order. Conversely, EF_{PM10} obtained for samples B, C and D were close to the values obtained upon wood combustion (Table 5.2). EF_{PM10} for sample A revealed the highest values, comparable to the value reported for the burning of rice straw.

EF of CO_2 (EF_{CO2}) for all residues studied in this work were similar to the EF_{CO2} published for the burning of wildland and scrubland fuels and are slightly higher than the

values estimated for wildfires in Portugal. EFs of CO (EF_{CO}) were very similar to those reported for wildfires, but were certainly higher than EF_{CO} derived from wildland and scrubland fuels.

5.3.2 PM organic components

In this work about 250 individual organic compounds were quantified in the smoke particles. Concentrations of organic compounds were normalised to OC (mass compound per mass OC). In general, the sum of identified compounds represented 10–20% of the OC mass, reaching 57% in $PM_{2.5}$ emitted from burning residue C. The distribution of several classes of chromatographically resolved organic constituents in smoke samples is provided in Figure 5.2. In general, phenolic compounds (0.2–39% OC w/w), acids (1.5–13% OC w/w) and alkenes (0.1–4 % OC w/w) were the major organic components identified and quantified in the solvent extractable fraction of smoke. In samples A and B, phenolic compounds and acids presented values of the same order in the fine and large ($PM_{>10}$) particulate fractions. However, aliphatic and polyaromatic hydrocarbons were much more abundant in $PM_{2.5}$ than in $PM_{2.5-10}$ and $PM_{>10}$ for all samples. Likewise, the concentration of organic acids was significantly higher in $PM_{2.5}$ than in $PM_{2.5-10}$ and $PM_{>10}$ for samples B and C. Nevertheless, non-extractable and/or non-chromatographically detectable organic compounds, including oligomeric humic-like substances and biopolymeric material, are expected to be the major part of organic matter that was not identified.

5.3.2.1 Homologous compound series

The OC-normalised mass concentrations of aliphatic and other individual compounds identified in this study are presented in annex as supplementary material (Table A3). The diagnostic parameters applied to the homologous series and PAHs are shown in Table 5.3. The distribution of *n*-alkanes in the smoke ranges in C chain length from C_{13} to C_{33}. On average, the total *n*-alkane OC-normalised concentrations in $PM_{2.5}$ were 8–14 times higher than in $PM_{>10}$ and $PM_{2.5-10}$, with the highest discrepancies being registered for samples B and C. The *n*-alkanes in $PM_{>10}$ of samples A, B and C maximise at C_{29} and C_{31}. In other fractions, diverse C_{max} were registered, varying from C_{16} to C_{23}. The carbon preference indices (CPI) for *n*-alkanes ranged between 1.6 and 3.6 (average=2.6), revealing an odd-to-even carbon number predominance.

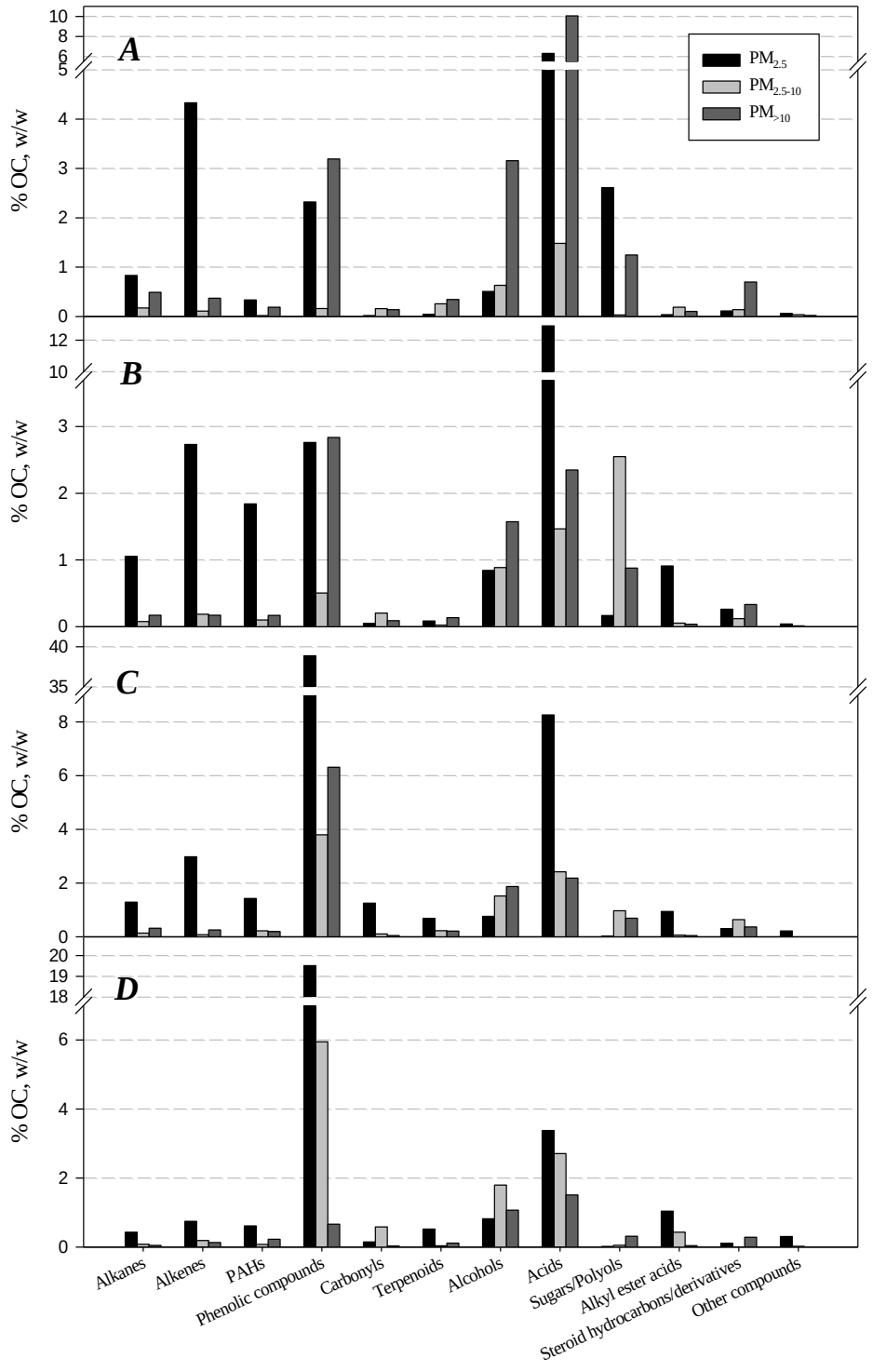

Figure 5.2 Contribution of chromatographically resolved organic compounds to OC in size-segregated particulate matter emissions.

Table 5.3 Homologous compound series found in the smoke (µg OC g^{-1}) and diagnostic parameters.

	Potatoes			Arable weed vegetation			Stalks of collard greens, etc			Container		
	$PM_{2.5}$	$PM_{2.5-10}$	$PM_{>10}$	$PM_{2.5}$	$PM_{2.5-10}$	$PM_{>10}$	$PM_{2.5}$	$PM_{2.5-10}$	$PM_{>10}$	$PM_{2.5}$	$PM_{2.5-10}$	$PM_{>10}$
Alkanes												
Total Alkanes	8329	1730	4886	10547	754	1705	12910	1351	3188	4313	830	498
Total *n*-Alkanes	871	122	4035	2103	275	1530	5882	783	2653	985	258	284
CPI C_{13-C34}			3.63	1.57		2.38	2.14	2.40	3.16			
C_{max}	C_{16}	C_{20}	C_{31}, C_{29}	C_{29}, C_{17}	C_{31}, C_{29}	C_{29}, C_{31}	C_{17}, C_{18}	C_{28}, C_{31}	C_{31}, C_{29}	C_{23}	C_{16}	C_{16}
UCM	335012	34231	36585	302671	16221	12202	479644	12693	2688	327844	71601	60958
U/R	6.7	10.8	4.6	8.3	6.3	3.8	9.4	12.2	0.6	25.8	28.1	34.6
Alkenes												
Total Alkenes	43307	1099	3689	27329	1862	1700	29820	770	2529	7466	1876	1301
Total *n*-Alkenes	11930	636	3023	12204	1157	1435	19135	602	2146	3265	1089	1223
C_{max}	C_{17}, C_{19}	C_{19}	C_{26}	C_{17}, C_{16}	C_{19}	C_{26}	C_{19}	C_{20}	C_{26}	C_{18}, C_{19}	C_{16}, C_{19}	C_{17}
n-Alkanols												
Total *n*-alkanol	3655	6272	25349	8002	8527	10296	6642	9834	8665	5427	17439	8746
CPI (C_{16}-C_{30})			4.78	5.91	10.89	4.32	8.43	5.64	6.01			5.39
C_{max}	C_{25}, C_{26}	C_{18}	C_{18}	C_{28}, C_{26}	C_{18}, C_{24}	C_{22}, C_{28}	C_{28}, C_{26}	C_{28}, C_{22}	C_{28}, C_{22}	C_{28}, C_{12}	C_{16}, C_{12}	C_{28}, C_{22}
PAHs												
Total PAHs	3095	165	986	14763	896	1281	6551	1759	1145	5294	727	1702
Total MePAHs	249	13	890	3630	100	404	7729	478	806	813	40	570
ΣPAHs	3344	177	1876	18393	996	1685	14280	2237	1951	6106	767	2271
Major PAHs	Phe, Ant	Nap, Phe	Phe, Nap	Py	Phe, Py	Phe, Py	Phe, Py	Py	Py	Phe, Flu	Phe, Flu	Phe, Py
Flu/(Flu+Py)	0.56	0.63	0.49	0.53	0.48	0.46	0.45	0.46	0.50	0.55	0.53	0.47
Phe/(Phe + Ant)	0.82	0.64	0.81	0.83	0.84	0.24	0.97	0.73	0.65	0.82	0.85	0.72
Bghi/Bap		0.03	0.09	0.26		0.61		1.00	0.10	0.02		
n-Acids												
Total n-acids	12205	7501	26239	20576	6384	10378	29310	4567	8103	8049	9401	5793
CPI C_{12}-C_{24}		12.68	52.54		15.97	43.67	30.06	19.22	34.66	50.13	39.33	41.52
C_{max}	C_{18}	C_{16}	C_{16}	C_{20}, C_{16}	C_{16}	C_{16}	C_{16}	C_{18}, C_{16}	C_{16}	C_{20}, C_{16}	C_{16}	C_{16}

This distribution confirms the contribution of epicuticular waxes from vegetation to *n*-alkanes (Oros et al., 1999). The dominant C_{29} and C_{31} *n*-alkane homologs often contribute up to 90% of all parafins found in plant waxes (Kolattukudy, 1970). In earlier studies, CPI values of the same order or higher in PM from burning of grasses (2.4–14) (Oros et al., 2006), rice (2) and wheat straw (12) (Hays et al., 2005) have been found. Taking into account that other sources, such as vehicular emissions and burning of plastics, produce CPI values lower or close to the unity (Alves, 2008), indices higher than 2 can be used in source apportionment studies to account for biomass burning emissions.

The *n*-alkene homologous series were in the range C_{12}–C_{35} and, similarly to alkanes, presented the highest concentrations in $PM_{2.5}$ of all samples. In samples A, B and C, C_{max} in $PM_{>10}$ was C_{26}, whereas in $PM_{2.5}$ and $PM_{2.5-10}$ it varied from C_{17} to C_{20}. The CPI for *n*-alkenes were in the range 0.31–1.26 (average=0.62), showing an odd-to-even carbon number preference. The *n*-alkenes are not abundant components in plant waxes and can be formed by the thermal dehydration of *n*-alkanols or, in minor amounts, released from oxidation of *n*-alkanes during incomplete combustion (Oros and Simoneit, 2001a).

An unresolved complex mixture (UCM) of branched and cyclic hydrocarbons, or "hump", was observed in all chromatograms of the aliphatic fraction (Table 5.3). UCM in the $PM_{2.5-10}$ and $PM_{>10}$ fractions of samples A, B and C revealed similar and relatively low values: 3.4–3.7, 1.2–1.6 and 0.2–1.2% of the OC mass, respectively. However, rather notable UCMs between 30 and 48% have been observed in the fine fractions of all samples. Since the UCM can be derived from incomplete combustion of lubricant oil (Boyer and Laitinen, 1975), its high levels in all fractions of sample D are rather predictable. Figure 5.3 shows chromatograms for the $PM_{>10}$ fractions of samples C and D, illustrating the differences in emission profiles when burning the same residues with and without the addition of a fossil fuel derivative. The ratio between chromatographically unresolved and resolved hydrocarbons (U/R) indicates the contribution of branched and cyclic hydrocarbons and can be used as a diagnostic parameter of the distribution of recent biogenic organic matter and anthropogenic materials in samples (Simoneit, 1985). Accordingly, the U/R of sample D, burned in a container with addition of used lubricant oil, was much higher than that of the same residue burned without addition of oil (sample C).

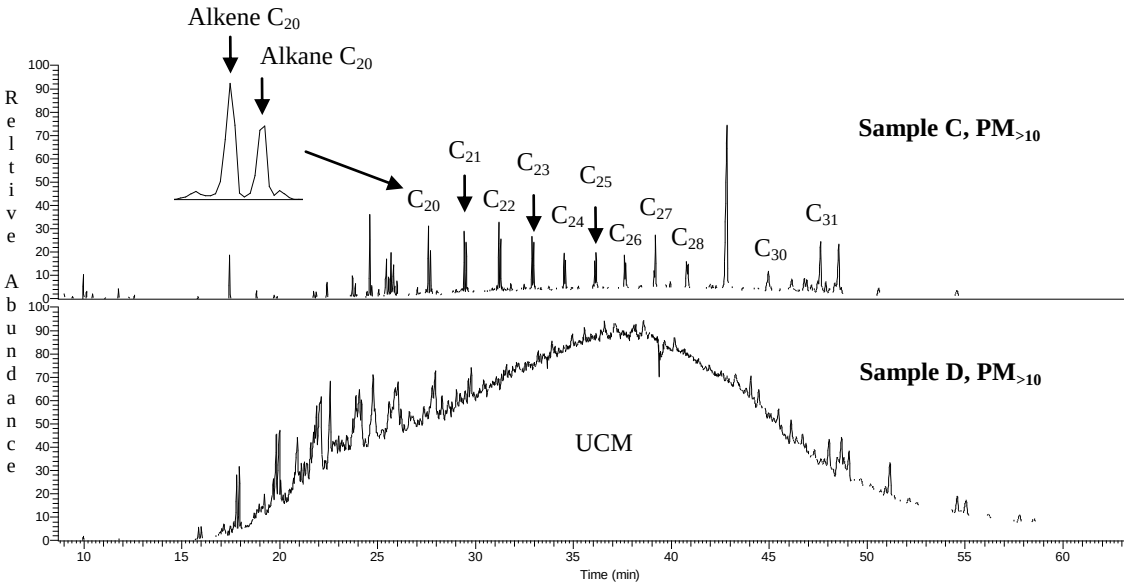

Figure 5.3 Chromatograms of the aliphatic fraction in $PM_{>10}$ from burning the same residue type with and without addition of lubricant oil.

The smoke samples revealed the presence of the C_6-C_{30} homologous series of *n*-alkanols (Table A3). The distribution of these homologs was characterised by a strong even-to-odd carbon number preference. CPI showed values between 4.3 and 10.8 (average=6.4), demonstrating the strong contribution from vegetation waxes. Depending on the sample, various C_{max}, in the range from C_{12} to C_{28}, were found. In general, alcohols represented about 0.6–0.9% of the OC mass in all samples, except in the $PM_{2.5}$ fraction of sample A (0.4% OC w/w) and $PM_{2.5\text{-}10}$ of sample C (1.7% OC w/w).

In general, carboxylic acids were the first or the second most abundant compounds in all samples. Similar features were reported for smoke from grasses (37.3%) by Oros et al. (2006), for Cape Jasmine smoke (37.7%) by Wang et al. (2009), and for smoke from burning leaves (Schmidl et al., 2008). In contrast, relatively low concentration of carboxylic acids were detected in $PM_{2.5}$ from cereal straw burning (Zhang et al., 2007) and in smoke from broad-leaf tree and shrub burning (0.8–9.0%) (Wang et al., 2009). The fraction of carboxylic acids included *n*-alkanoic homologs, unsaturated fatty acids, oxy- and hydroxyacids and dicarboxylic acids (Table A3). The relative abundance of carboxylic acids is depicted in Figure 5.4. A series of *n*-alkanoic acids were identified in the smoke, ranging from C_6 to C_{24} and showing a typical pattern for samples of biogenic origin with a strong even-to-odd carbon number preference. CPI values oscillated between 12.7 and 50.1 and maximise at C_{16}.

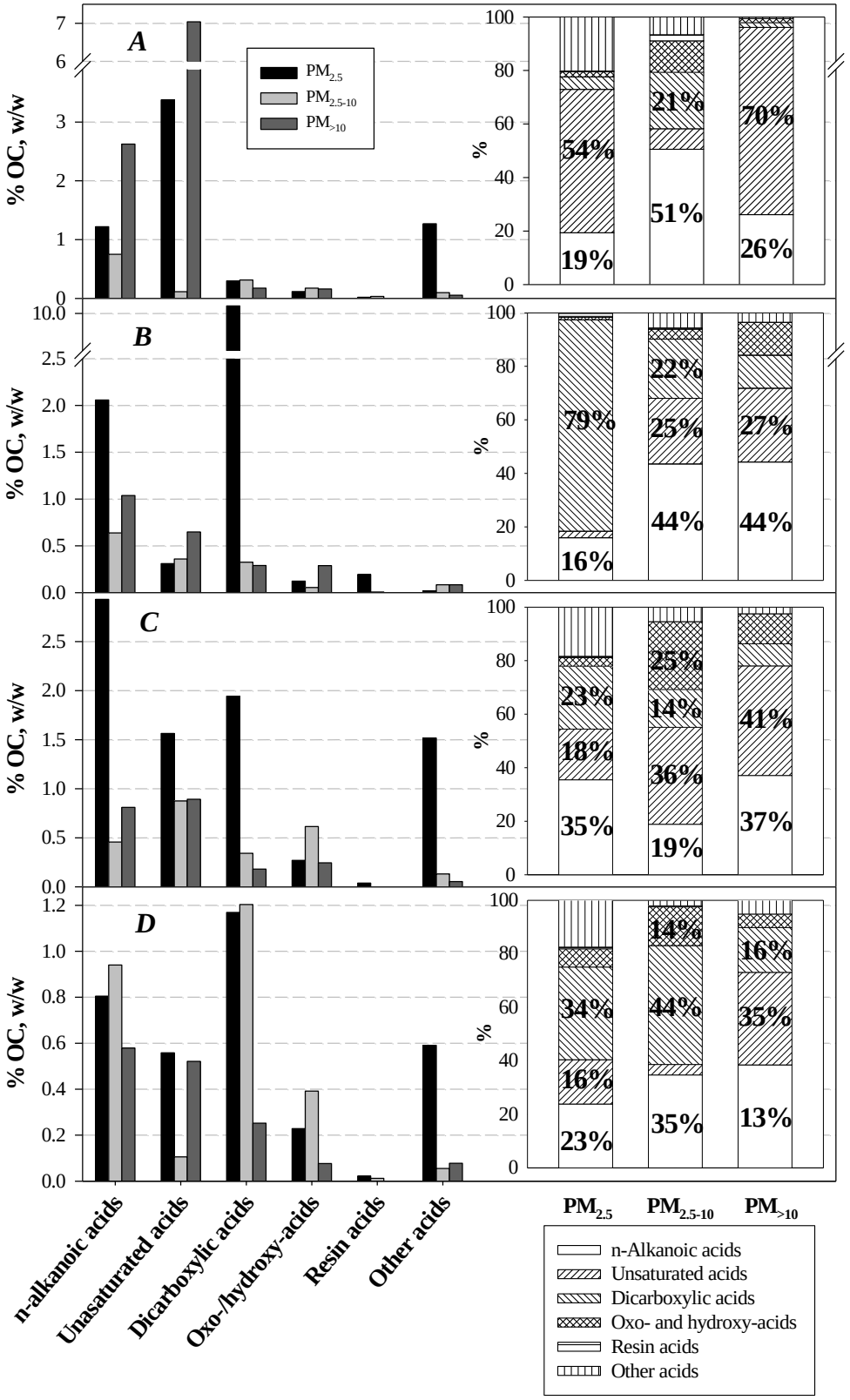

Figure 5.4 Contribution of organic acids to OC (left panels) and their relative distribution (right panels).

These CPI values are higher than those reported in previous studies, namely, 6.9–18.8 for grass smoke (Oros et al., 2006) and 11.3 for cereal straw smoke (Zang et al., 2007). *n*-Alkanoic acids are basic units of plant fats, oils and phospholipids (Simoneit 2002; Wang et al., 2009). With the exception of the $PM_{>10}$ fraction of sample A and the $PM_{2.5}$ fraction of sample C, for which the acid content is higher, the *n*-alkanoic normalised-OC concentrations ranged from 0.5 to 1.2% in all samples. Palmitic acid (hexadecanoic acid) was detected as a predominant compound, representing, on average, 22, 31 and 51% of the total *n*-alkanolic acid mass in the $PM_{2.5}$, $PM_{2.5-10}$ and $PM_{>10}$ fractions of all samples, respectively. Some distinguishable tendencies in the relative contribution of these compounds to the various PM fractions are shown in Figure 5.4.

Dicarboxylic acids were represented by the C_3-C_{11} homologs with C_{max} at C_7. These were, in general, less abundant (0.2–1.2% OC) compared to *n*-alkanoic acids, though in $PM_{2.5}$ of samples B and C the concentrations of dicarboxylic acids reached 10.2 and 1.9% of the OC mass, respectively. It should be stressed that dicarboxylic acids represented 79% of the total amount of acids in $PM_{2.5}$ from sample B. Dicarboxylic acids may be formed from unsaturated lipids through a series of autoxidation reactions (Rogge et al., 1991) and have been associated with several emission sources (Legrand et al., 2007; and references therein). Significant amounts of dicarboxylic acids were also detected in the particulate fine fraction of smoke from burning of cereal straw (Zhang et al., 2007), rice and wheat (Hays et al., 2005) and foliar fuels (Hays et al., 2002).

Unsaturated and polyunsaturated carboxylic acids are important components of plant oils (Lísa et al., 2009). These constituents were detected in appreciable amounts, accounting for 3.4% and 7.0% of the OC mass in $PM_{2.5}$ and $PM_{>10}$ of sample A, respectively, while the percentage was 1.6% in $PM_{2.5}$ of sample C. Oleic acid (octadecenoic acid) and linoleic acid (octadecadienoic acid) were the most abundant compounds (Table A3).

Some *n*-alkan-2-ones and minor *n*-alkanals with odd carbon number were found in the smoke samples. The *n*-alkan-2-ones are thermal alteration products of aliphatic precursors, such as *n*-alk-1-enes, which oxidise via the secondary alkanol intermediate to the ketones (Leif and Simoneit, 2000; Simoneit, 1978). On average, carbonyl compounds represented 0.08% of the OC mass in all samples, excluding in the $PM_{2.5}$ fraction of sample C and in $PM_{2.5-10}$ of sample D. In these latter samples, carbonyl compounds

contributed to 0.84 and 0.55% of the OC mass, respectively. Oros et al. (2006) reported the presence of a homologous series of *n*-alkan-2-ones at notable amounts in the smoke from cotton grass and pampas grass.

A series of alkanoic acid methyl esters in the C range from C_{14} to C_{26} were detected in minor amounts, representing, on average, 0.05% of the OC mass. Only in $PM_{2.5}$ of sample C, the acid methyl esters accounted for 0.94% of the OC mass.

5.3.2.2 Polycyclic aromatic hydrocarbons (PAHs)

PAHs are commonly formed upon thermal decomposition of organic matter and any biomass burning causes their formation to some extent. About 30 individual PAHs were identified in the smoke samples. The total OC-normalised concentrations of all PAHs (ΣPAHs) were in the range 177-18393 μg g^{-1} OC, presenting, in general, higher amounts in $PM_{2.5}$ of all smoke samples (Table 5.3). The predominant PAHs were phenanthrene, pyrene, fluoranthene and anthracene. The highest concentrations of these PAHs were registered in $PM_{2.5}$ of sample C, in which they accounted for 0.2-0.8% of the OC mass. The ratios of certain PAHs are rather specific for each kind of burning source and may be employed as diagnostic parameters to investigate their specific origin (Bi et al., 2003; Gogou et al., 1996). The Flu/(Flu + Pyr) ratios ranged from 0.46 to 0.63 for all residues studied (Table 5.3). These ratios are similar to those reported for smoke from burning of cereal straw (0.50–0.53) (Hays et al., 2005), broad-leaf trees (0.50–0.55) and shrubs (0.54–0.60) (Wang et al., 2009), grasses (0.53–0.63) (Oros et al., 2006), and a shrub-dominated forest (0.6 for $PM_{2.5}$ and 0.56 for $PM_{2.5-10}$) (Alves et al., 2010a). Generally, the Phe/(Phe + Ant) ratios fluctuated between 0.65 and 0.85, lying in the ranges reported in the above-mentioned studies: 0.70–0.83 for broad-leaf trees, 0.71–0.76 for shrubs, 0.70–0.63 for grasses and, 0.75 in $PM_{2.5}$ and 0.75 in $PM_{2.5-10}$ for a shrub-dominated forest smoke samples. The Bghi/BaP ratios calculated for open burning of stalks of collard greens (sample C) were 0.19–0.24. However, this ratio increased to 0.31–0.35 when the same type of residue was burned in a container with addition of used lubricant oil. Comparatively, higher Bghi/BaP ratios have been reported for emissions from diesel (1.2–2.2) and gasoline (2.5–3.3) cars, and from road dust (0.91). Lower ratios (0.02–0.06) were obtained for industrial emissions (Rogge et al., 1993; Yang et al., 1998). The Flu/(Flu + Pyr) ratios assigned to the same sources were 0.60–0.70, 0.40 and 0.21–0.26, respectively. Since

PAHs are emitted by diverse anthropogenic sources (Oros and Simoneit 2000, 2001a,b; Simoneit, 1998), they cannot be documented as exclusive markers for biomass combustion. However, in general, the diagnostic ratios from biomass burning can be easily differentiated from those of other combustion sources.

5.3.2.3 Phenolic compounds

Phenolic compounds (PHC) were found to be significant contributors to the organic fraction of particulate matter. This group of compounds was previously detected as the most abundant in smoke from burning of samak (Theaceae family) (67.1% of all identified organic matter) and as the second most abundant in smoke from other Chinese broad-leaf trees and shrubs (23.5–38.0%) (Wang et al., 2009). Methoxyphenols (MP) were predominant species in wheat and corn straw smoke (Zhang et al., 2007). Significant amounts of PHC (around 11% of total resolved components) were detected in the smoke from the burning of grasses (Oros et al., 2006). PHC were detected as dominant constituents in the smoke from samples C and D and as the second major group for samples A and B (Figure 5.5). In $PM_{2.5}$, PHC accounted for about 40% and 19% of the OC mass in samples C and D, respectively. This group included polyphenols, methoxyphenols and, in minor amounts, alkyl phenols. Methoxyphenols are essentially emitted from the oxidation/pyrolysis of lignin (Hawthorne et al., 1988). Lignin, along with cellulose and hemicellulose, is a major component of vegetation and responsible for the strength and rigidity of plant stems. The oxidation and pyrolysis products can be classified as regards their origin into three general groups: coumaryl, vanillyl (guaiacyl) and syringyl compounds (Simoneit et al., 1993). The yield of these three groups of compounds usually differs for different biomass species. For instance, the smoke from combustion of softwoods contains predominantly guaiacyl-type compounds, while hardwood and shrubs burning smoke possesses a mixture of guaiacyl- and syringyl-type MP (Hawthorne et al., 1988, 1992; Nolte et al., 2001; Simoneit, 2002; Simoneit et al., 1993). However, for grass smoke, the abundance of MP are variable, depending on the type of species. Coumaryl derivatives were the most abundant MP found in tundra grass and sugarcane smoke, whereas substituted syringyls were the predominant group in mixed ryegrass and bamboo smoke.

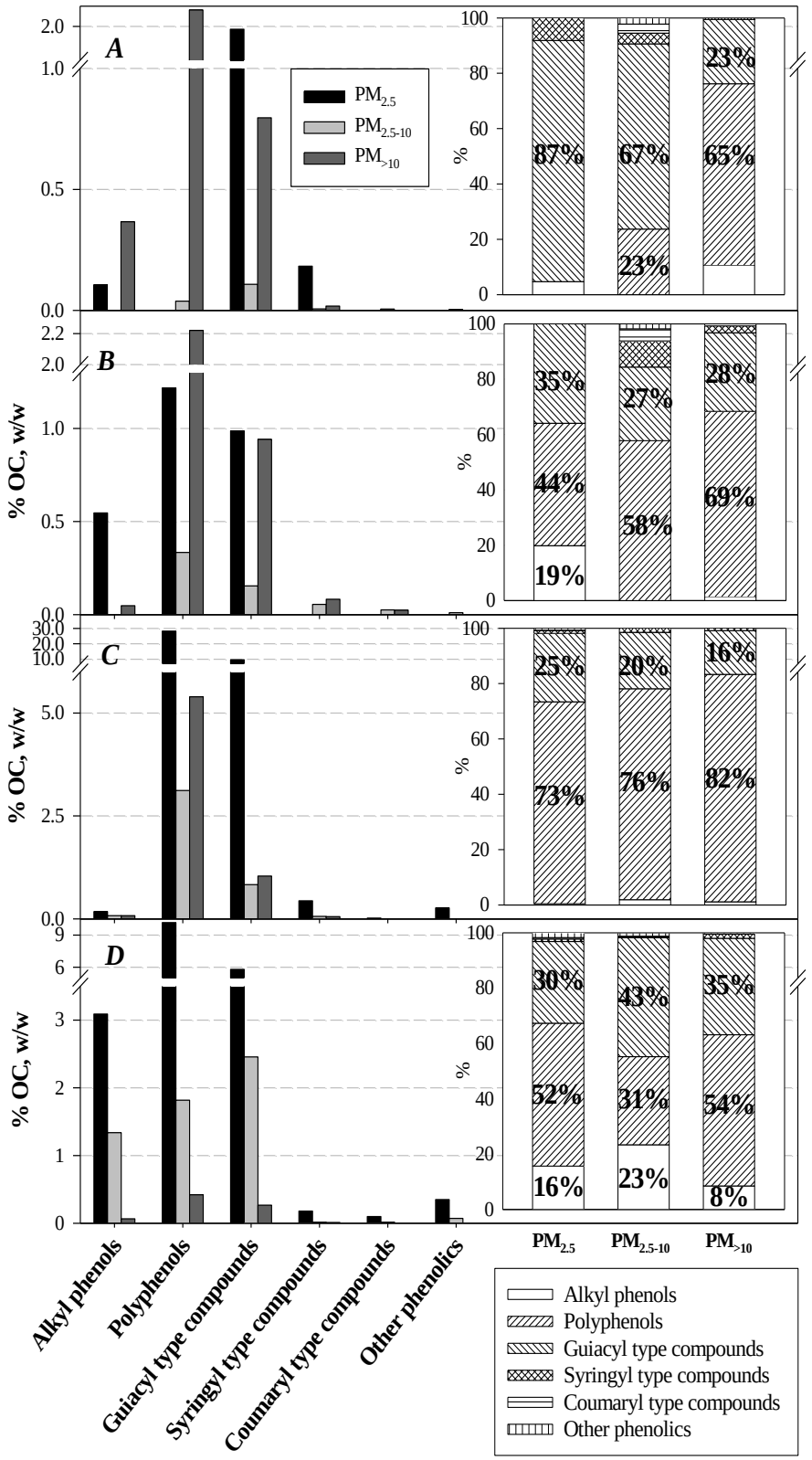

Figure 5.5 Contribution of phenolic compounds to OC (left panels) and their relative distribution (right panels).

On the other hand, cotton grass smoke contained essentially the guaiacyl compounds (Oros et al., 2006). Similar proportions of syringyl- and guaiacyl-type derivatives were observed in the smoke of wheat and rice straws (Hu et al., 2002).

The contribution of different PHC to OC and their relative occurrence in PM fractions are shown in Figure 5.5. In general, MP were the major phenolics in $PM_{2.5}$ of all smoke samples. Guaiacyl-type derivatives contributed to 67–87% of PHC in $PM_{2.5}$ of sample A and to 16–43% OC w/w of all fractions in other samples. Among the ten identified guaiacyl pyrolysis products, vanillin and isoeugenol were the most abundant, especially in $PM_{2.5}$ from samples C and D, contributing to 3.1–4.4 and 0.6–5.6 mg g^{-1} OC, respectively. The particularly pronounced mass concentrations of PHC in samples C and D are not surprising taking into consideration that those smoke samples derived from the burning of fine branches of deciduous woods, which have a relatively high content of lignin and tannins. Besides lignin, tannins may be considered as important contributors to the polyphenol content in the aforementioned samples. In fact, polyphenols in the fine particulate fractions of samples C and D were much more abundant (30 and 9.5 % w/w OC, respectively) than in samples A and B (Figure 5.5). Among polyphenols, cathehols and methyl cathehols were predominant. The syringyl (mainly syringic aldehyde, syringic and sinapic acids) and coumaryl (mainly *p*-cresol) structures were rather scarce in the emitted smokes (Figure 5.5). It is noteworthy that the emission of polyphenols is vulnerable to the burning technique and the addition of an anthropogenic residue (samples C and D). Thus for the same agricultural waste the addition of used lubricant oil led to the substantial diminishing of polyphenols in emitted smoke (Figure 5.5). Simultaneously to decreased polyphenolic emissions, the emission of alkyl phenols increased drastically indicating an eventual anthropogenic source of these pyrolysis products.

5.3.2.4 Biomarkers and other products

Oxo- and hydroxyacids such as lactic, levulinic, glycolic and hydroxybutyric acids were detected in all smoke samples. Levulinic and glycolic acids may be derived from hydrolysis of hemicelluloses (Girisuta, 2007). In addition, noticeable contributions to OC of aromatic acids, such as benzoic acid, ferulic acid, cinnamic acid and phthalic acid, were also observed.

Sterols and terpenoids constitute some of the biomarker compounds identified in this study. Sterols are ubiquitous and typical constituents of all plants. These high molecular weight compounds may be volatilised directly into smoke (Abas et al., 1995; Simoneit, 2002; Simoneit et al., 1993). The most abundant sterol in all smoke samples was *β*-sitosterol, followed by lower abundances of campesterol and stigmasterol. The higher concentrations of *β*-sitosterol relative to stigmasterol were previously observed in grass smoke (Oros et al., 2006), wheat straw smoke (Hays et al., 2005) and cereal straw smoke (Zhang et al., 2007). Several products of thermal alteration from sterol precursors were identified in minor amounts in some smoke samples and include stigmastan-3,5-diene, stigmastan-4,5,22-triene, and stigmastan-3,5,22-triene. Other steradienes, whose individual identification was not possible, were present in all the smoke samples, especially in the fine particulate fractions, where the mass concentrations ranged from 56 to 455 µg g^{-1} OC.

Phytol, a common terpenoid found in all plants, was observed in significant amounts, showing highest concentrations in all particulate fractions of sample C (Table A3). Another abundant terpenoid was eucalyptol. It presented especially high concentrations in $PM_{2.5}$ from samples C and D.

5.3.2.5 Saccharides and polyols

Among the identified sugar derivatives, levoglucosan was the dominant compound (Table A3). The maximum mass concentration values were recorded in $PM_{>10}$ (0.8% OC, w/w) and $PM_{2.5-10}$ (2.5% OC, w/w) of sample B. In all other samples, the highest concentration of levoglucosan was found in $PM_{>10}$. This result is in agreement with the size-resolved anhydrosugar composition in smoke aerosol from controlled field burning of rice straw obtained by Engling et al. (2009) and Lee et al. (2008). Probably, the thin layers of soil slowly burn together with the agricultural/garden residues at relatively low temperatures. Such distinct burning conditions for these residues, compared to other types of biomass, may result in soil and ash particles, which are usually more coarse, to be elevated during the burning process by the convective processes over the flame and subsequently be suspended. On the other hand, the high ambient relative humidity during the burning experiments may have contributed to water uptake by the smoke particles in addition to other atmospheric processes (e.g. coagulation), shifting the organic tracer distribution to coarser sizes (Lee et al., 2008).

Levoglucosan is a product from the pyrolysis of cellulose (Simoneit et al., 1999), the most abundant polysaccharide in plant materials, and its domination is not surprising. In comparison with other biomass burning emissions, such as wheat and rice straw (Hays et al., 2005), shrubland fires (Alves et al., 2010a), Amazonian forest fires (Graham et al., 2002) and woodstove combustion for heating purposes (Gonçalves et al., 2010), the levoglucosan-to-OC ratios for agriculture/garden residue burning were lower, which should be taken into account in source apportionment studies. Is has been observed that the cellulose (the levoglucosan precursor) content change along the stalks/branches of the plant raw materials. There is a general tendency for a decrease in cellulose as we move from the base of the stalks or branches to the top, since mature tissues (at the base) accumulate higher amounts of metabolic products than the younger parts at the top (Ververis et al., 2004). Thus, it is expected to have lower levoglucosan emissions from burning branches and leaves than from wood tissues. Mannosan, another anhydrosugar emitted upon burning of agriculture wastes, was detected in appreciable amounts only in $PM_{>10}$ (0.01% OC, w/w) and $PM_{2.5-10}$ (0.07% OC, w/w) of sample C. Monomeric sugars were detected in the PM fractions of all examined samples, revealing rather moderate mass concentrations (0.01–0.08% OC, w/w) with the exception of $PM_{2.5}$ in sample B, in which the sugars represented 0.16% of OC mass.

Inositol isomers were the most abundant polyols. They were present essentially in $PM_{2.5}$ (ca 2.4% OC, w/w) and $PM_{2.5-10}$ (0.02% OC, w/w) of sample A (potatoes haulm). In vegetation, inositol is found as phytic acid (inositol hexaphosphate), which is the main storage form of phosphorus in many plant tissues, especially bran and seeds (Mallin, 2003). Inositol, a derivative from phytic acid, was reported previously for potato tubers and haulm (Shaw, 1969). Hence, the presence of this polyol in the smoke from potato haulm may result from the thermal decomposition of phytates. In effect, inositol may be considered as a tracer for the smoke of the aforementioned agricultural residues.

5.4 Conclusions

The analysis of size-segregated particulate matter ($PM_{2.5}$, $PM_{2.5-10}$ and $PM_{>10}$) emitted from the burning of three types of agricultural/garden residues allowed the discrimination of the carbonaceous content and the identification and quantification of about 250 compounds of different organic classes. The $PM_{>10}$ concentrations were

significantly higher when compared to fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) fractions for all samples. Probably, due to the high relative humidity conditions during sampling, formation of larger particles from fog processing may have occurred. The addition of lubricant oil to the agricultural/garden wastes as a co-fuel enhanced considerably the $PM_{2.5-10}$ emissions. Regardless of the particle size or waste type, the carbonaceous fraction was dominated by organic carbon (OC/TC~98%). Despite distributions patterns of organic compounds in PM varied among residues, the amounts of phenolics (0.2–39% OC, w/w) and organic acids (1.5–13% OC, w/w) were always predominant over other organic compounds in the organosoluble fraction of smoke. The phenolic fraction was composed predominantly of polyphenol and guaiacyl derivatives. PAHs were detected in relatively small amounts. Their molecular diagnostic ratios were similar to those reported for smoke from other agriculture residues and different from those reported for other combustion sources, indicating that they can be applied as a source apportionment tool. Among biomarkers, levoglucosan, β-sitosterol and phytol were detected in appreciable amounts in the smoke of all agricultural/garden residues. In addition, inositol may be considered as an eventual tracer for the smoke from potato haulm burning.

This work highlighted that the relative contribution of different carbon forms and particular classes of organic compounds depend on atmospheric conditions, size fraction of particles emitted from burning and type of wastes. Hence, the analysis of just one size fraction of particulate matter may not be enough to assess the global emission and may not always truly reflect the emission profiles of individual organic components. Since rather high fractions of some organic tracers were observed in very coarse particles ($PM_{>10}$), possibly due to the influence of various atmospheric processes, including coagulation of fresh smoke particles, it should be taken into account that, in addition to different types of biomass burning, the particular conditions associated with specific practices contribute to unique emission patterns.

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CHAPTER 6

Chapter 6. Particulate organic compounds emitted from experimental wildland fires in a Mediterranean ecosystem

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Abstract

Fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) smoke particles from controlled biomass burnings of a shrub-dominated forest in Lousã Mountain, Portugal, enabled the quantification by chromatographic techniques of several molecular tracers for the combustion of Mediterranean forest ecosystems, which could be conducive to source apportionment studies. The major organic components in the smoke samples were pyrolysates of vegetation cuticles, mainly comprising steradienes and sterol derivatives, carbohydrates from the breakdown of cellulose, aliphatic lipids from vegetation waxes and methoxyphenols from the lignin thermal degradation. Most of these compounds are chiefly found in fine particles. Polycyclic aromatic hydrocarbons (PAH) were also present as minor constituents. Anhydrosugar and PAH molecular diagnostic ratios were applied as source assignment tools. Some biomarkers are reported for the first time in biomass burning smoke.

Keywords: forest fires, smoke particles, OC, organic speciation, tracers.

6.1 Introduction

Forest fire areas burned worldwide have increased in recent decades resulting in a significant source of carbonaceous particulate matter with a profound effect on the carbon cycle (Ito, 2005) and on atmospheric chemistry (Antilla et al., 2008; Junquera et al., 2005; Pfister et al., 2008a; Yokelson et al., 2007). These carbonaceous aerosols have climate-forcing impacts, either contributing to or counterbalancing the effects of greenhouse gases (Pfister et al., 2008b). In particular, elemental carbon particulate matter (EC) has recently been identified as an important contributor to radiative heating of the atmosphere (Jacobson, 2001). Organic carbon particulate matter (OC), which is emitted along with EC, has a cooling effect on climate and may act to offset some of the global warming impact of EC emissions (Penner et al., 1998). In the case of aerosols from biomass burning, OC is thought to totally balance the warming potential of EC, because these emissions are characterised by high OC/EC ratios (Schaap and Denier van der Gon, 2007; and references therein). In addition to being able to perturb climate and atmospheric chemistry, smoke aerosols possess a toxicity level greater than that of an equivalent dose of particulate matter in ambient air (Wegesser et al., 2009).

While the inorganic composition of the smoke particles and the corresponding emission factors have been estimated in a few number of previous studies (Andreae et al., 1998; Ferek et al., 1998; Nance et al., 1993; Yamasoe et al., 2000), the molecular speciation of organic aerosols in wildland fire plumes is very sparse (Lee et al., 2005; Yan et al., 2008). Organic matter represents the major fraction of smoke aerosols, sometimes accounting for over 90% of the total mass (Graham et al., 2002, 2003; Yamasoe et al., 2000). This type of material comprises an extremely complex assortment of compounds rendering comprehensive characterisation at a molecular level very tricky. Additionally, unlike other sources, wildland fire emissions of particulate organics are poorly quantified in the literature due to the difficulties in estimating their temporal and spatial distribution. Thus, information on the emission of organic products of biomass combustion refers almost exclusively to laboratory-based studies designed to simulate domestic burning for space heating (e.g. Fine et al. 2004; Iinuma et al., 2007; Schmidl et al., 2008). However, it is known that different biofuels and combustion processes can produce different mass emission rates and organic compound source signatures (Fine et al., 2004; Pio et al. 2008). Given that emission factors are required for modelling atmospheric processes, inventories,

and source apportionment studies, it is desirable to establish more precise information reflecting country and regional conditions. Aiming to help fulfilling the gap that exists in the Mediterranean, a detailed organic characterisation of smoke emissions from a Portuguese shrub-dominated forest is presented in this study.

6.2 Experimental

In May 2008, seven experimental fires have been conducted at a shrub-dominated forest in Lousã Mountain (~ 40º04'38''N and 08º09'35''W), central Portugal. The vegetation cover was composed by some isolated pine trees (*Pinus pinaster*) and a continuous mass of dwarf Spanish heath (*Erica umbellata*), Spanish heather (*Erica australis*) and prickled broom (*Chamaespartium tridentatum*), with an average moisture content of 43.7%, heights between 54 and 104 cm, a bulk density of 2.7 kg m^{-3} and a fuel load of 27.7 ton ha^{-1}. These three shrub species are classified as angiosperms. A tripod high-volume sampler (TE-5200, Tisch Environmental Inc.) operating at a flow of 1.13 m^3 min^{-1} was used to collect sequentially, on pre-baked quartz fibre filters, coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$) smoke particles. The impaction system for capturing PM_{10} was designed at the University of Aveiro in accordance with the Marple and Rubow's theory (1986). Sampling was performed at 1.5 meters above ground, downwind from the burning area, at distances of 20–200 meters from the flame. The samplers were connected only when impacted by the smoke plume.

The carbonaceous content (EC and OC) of particulate matter was analysed by a thermal–optical technique (Alves et al., 2010a). Two 9 mm diameter filter punches, in the case of $PM_{2.5}$ samples, or strips representing 1/20 of the total area, in the case of $PM_{2.5-10}$ samples, were used in each analytical run. For each filter, two or three replicate analyses were done. The analytical procedure for the determination of cellulose in atmospheric aerosols included an enzymatic conversion of total cellulose to D-glucose followed by its photometric detection (Sánchez-Ochoa et al., 2007). Two filter punches (2.5 cm in diameter) and one strip (1/10 of total filter area), were used for extracting cellulose from fine and coarse particulate matter samples, respectively. The determination of levoglucosan, other sugars and polyols was performed by high-performance liquid chromatography with an electrochemical detector (Dionex ED40, pulsed amperometry with gold working electrode) (Caseiro et al., 2007), using the same filter areas as described

for cellulose. The remaining parts of the filters were solvent extracted and analysed by gas chromatography – mass spectrometry (GC-MS) after fractionation of the organic extracts by flash chromatography and appropriate derivatisation techniques (Alves et al., 2010a; Oliveira et. al., 2007). Compound identification was made by comparison with authentic standards, matching against the Wiley mass spectral libraries and analysis of fragmentation patterns. Every organic extract was injected in triplicate (3 different dilutions), consecutively in the single ion monitoring and total ion chromatogram modes. The GC-MS calibration was based on a total of about 300 standards (Sigma-Aldrich, TSI and Chiron) in five different concentration levels with relative response factors (RRF) determined individually to the majority of compounds. For those compounds for which no authentic standards were available, relative response factors were calculated as an average of the relative response factors from the overall homologous series or from compounds of similar chemical structure and retention time.

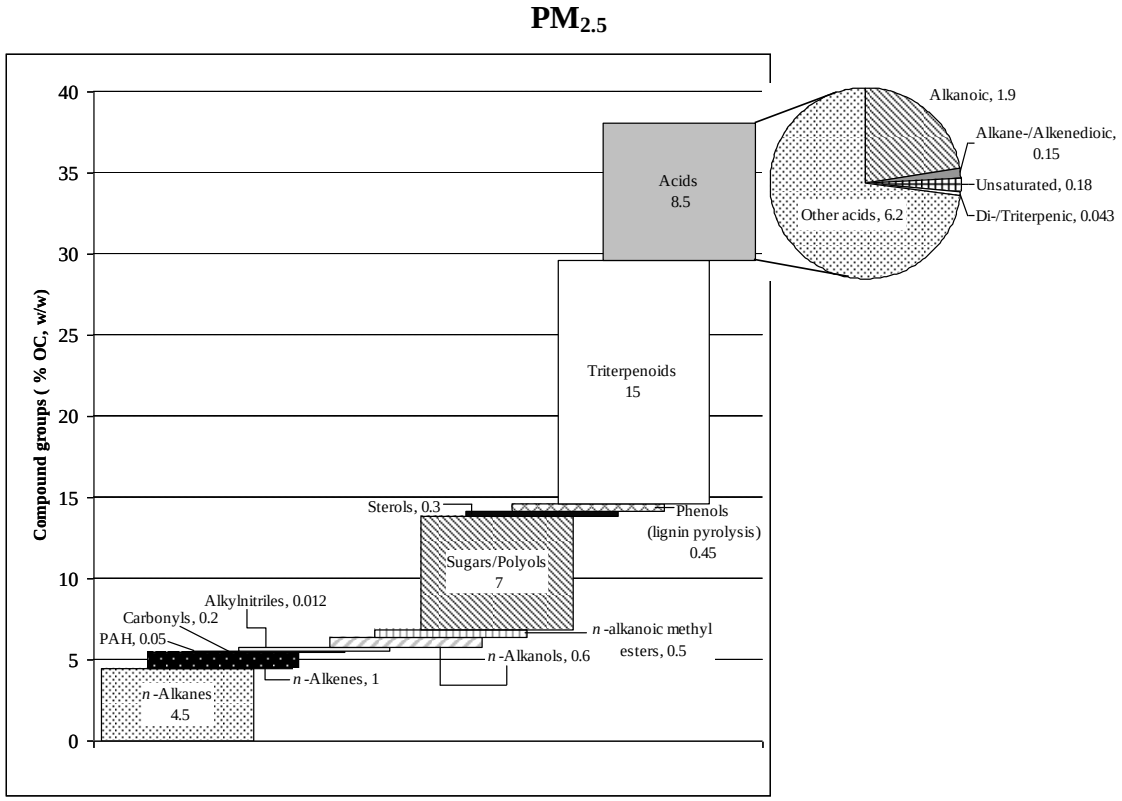
Additional information concerning Fourier transform infrared spectrometry gas measurements of the smoke plumes from the shrubland fires, as well as the detailed inorganic particle composition, can be found in Alves et al. (2010b). It should be noted that, from the increments of CO and CO_2 concentrations in relation to background levels, an average modified combustion efficiency (MCE = $\Delta CO_2/(\Delta CO_2+\Delta CO)$) of 0.99±0.01 was obtained, clearly suggesting a predominance of flaming combustion for the seven burning tests. Among other factors, the low degree of fuel packing may have contributed to such high MCE values (Alves et al., 2010b). It should be stated that, since these fires have been applied in a knowledgeable manner under selected weather conditions to achieve programmed research objectives, the chemical composition of their emissions may differ appreciably from wildfires.

6.3 Results and Discussion

6.3.1 Carbonaceous content of particles and distribution of major compound groups

The $PM_{2.5}$ and $PM_{2.5-10}$ smoke samples presented concentrations in the ranges 600-12500 μg m^{-3} and 221–1135 μg m^{-3}, respectively. These samples were very rich in OC, accounting for almost 100% of the total carbonaceous content. The OC mass fractions in particles (~ 40–60% w/w) were in the range of values published for biomass burning in

grass, savannah, cerrado, boreal and tropical forests (Reid et al., 2005). On average, the OC concentrations were 46-fold higher in $PM_{2.5}$ than in $PM_{2.5-10}$, whereas inorganic species were more concentrated in the coarse size (Alves et al., 2010b). Thus, in spite of many pyrogenic organic compounds being emitted at higher levels in the fine fraction typical of smoke, the coarse mode may be characterised by a higher OC-normalised concentration of these constituents. The mean OC emission factor in these prescribed burnings in Lousã Mountain was estimated to be 1.1 g kg^{-1} of fuel burned, on a dry basis (Alves et al., 2010b). The relative distribution of all identified organic compounds in the natural vegetation burning smoke is provided in Figure 6.1. The chromatographically resolved organics were dominated by triterpenoids, acids, sugars and aliphatic compounds, accounting for 38 and 18% of the OC mass in the fine and coarse particles, respectively. The organic compounds that were not extractable or not detectable by GC-MS, such as oligomeric humic-like substances and biopolymeric material, likely represented a major fraction of the unidentified organic matter.



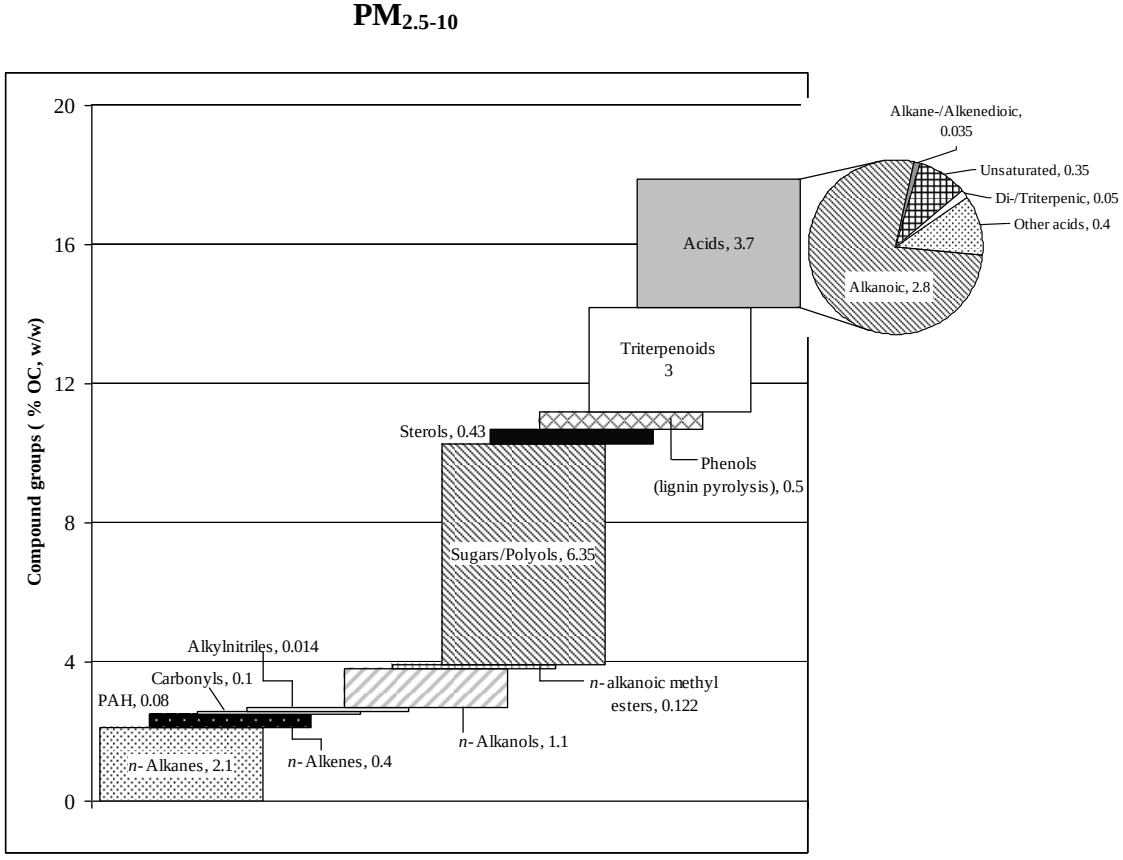


Figure 6.1 Contribution of chromatographically resolved organic compounds to OC in the fine and coarse particle emissions.

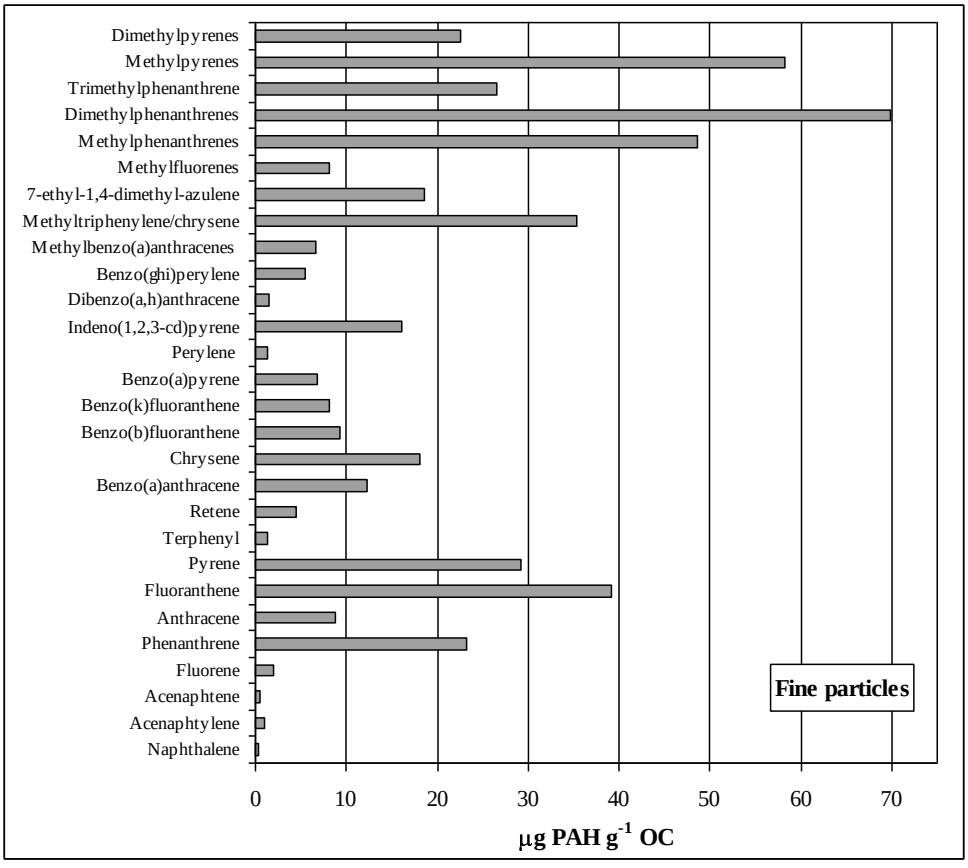
6.3.2 Homologous series and polyaromatic hydrocarbons

The distribution of the *n*-alkane homologous series ranged from C_{17} to C_{33} and from C_{12} to C_{33} in $PM_{2.5}$ and $PM_{2.5-10}$, respectively, maximising at C_{29} and C_{31}. The CPI of the coarse particles (14.6) was much higher than that of fine particles (2.08). Vascular plants synthesise epicuticular waxes enclosing odd carbon number homologs generally in the C_{25}-C_{33} range peaking at C_{29} and C_{31}, which often represent up to 90% of all alkanes detected in vegetation waxes (Oros and Simoneit, 2001b). On average, these paraffinic compounds accounted for 4.5% and 2.1% of the OC mass in fine and coarse particles, respectively. Variable CPI values have been found in aerosols from burning of deciduous trees (3.69–35.66) (Oros and Simoneit, 2001b), grasses (2.40–14.00) (Oros et al., 2006), rice (2) and wheat straw (12) (Hays et al., 2005), and broad-leaf trees and shrubs from South China (1.16–2.87) (Wang et al., 2009). As evidenced by the whole range carbon preference index

values, the *n*-alkane distributions in the emissions vary noticeably by fuel type, fuel age, species biochemistry, and growth environment (Hays et al., 2005). However, all the values were higher than those reported for catalyst-equipped gasoline-powered (0.88) and noncatalyst-equipped gasoline-powered motor vehicles (0.77) (Schauer et al., 2002). Thus, high values of CPI may be used to differentiate biomass burning from fossil fuel emissions.

The *n*-alkene homologs were in the range C_{12}-C_{32}, maximising in general at C_{20}, C_{22}, C_{24} or C_{26}, and accounting for 1.0% and 0.4% of the OC mass in fine and coarse particles, respectively. The *n*-alkenes found in smoke samples were for the most part terminal olefins (i.e. alk-1-enes). Since they are not major constituents of plant waxes, it has been speculated that olefinic compounds may be formed by the thermal dehydration of *n*-alkanols and, to a lesser extent, from *n*-alkanes by oxidation during incomplete combustion (Oros and Simoneit, 2001b).

The major PAH found in smoke particles were alkylated compounds, benzo(a)anthracene, pyrene, phenanthrene, fluoranthene and chrysene (Figure 6.2).



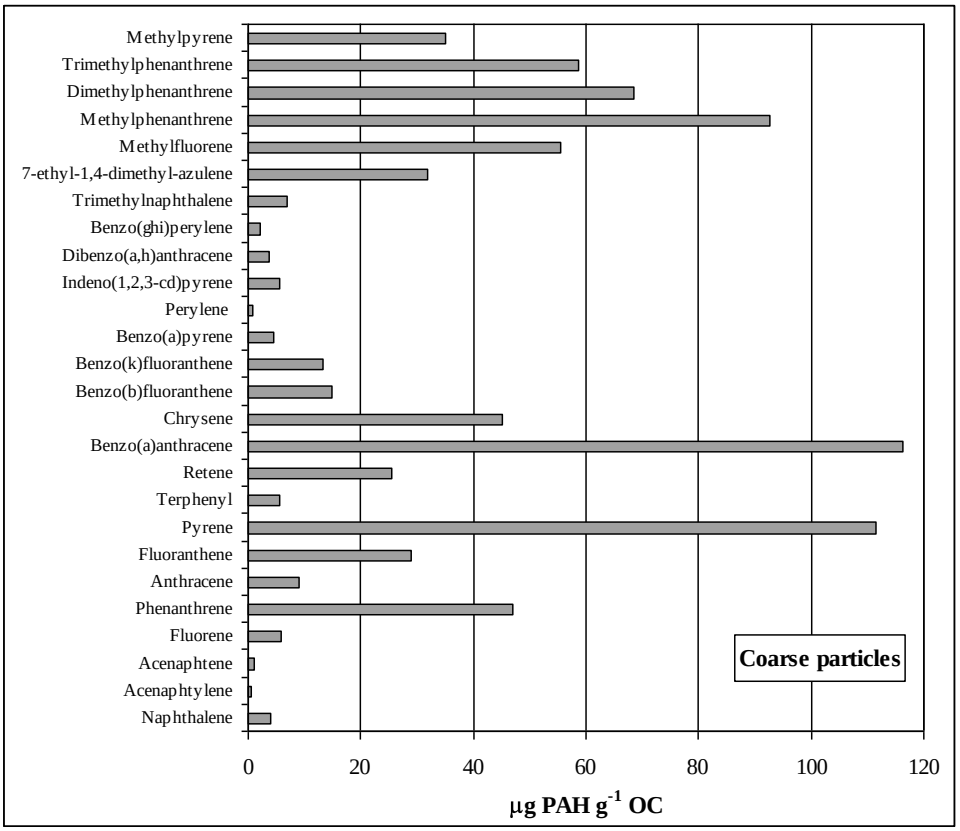


Figure 6.2 Normalised particulate OC emissions of PAH species (Based on the EPA 610 PAH calibration mix).

In general, these pyrogenic components presented higher concentrations in the fine fraction of particulate matter, although the coarse fraction revealed a higher OC-normalised content. Contributions of carcinogenic USEPA priority polyaromatic hydrocarbons (Alves, 2008) represented 2.5 and 2% of the PAH total concentrations in $PM_{2.5}$ and $PM_{2.5-10}$, respectively. In spite of assignment to a specific combustion source being difficult, the application of PAH diagnostic ratios have been used to investigate their origin in the atmosphere (Wang et al., 2009). The ratios of fluoranthene to fluoranthene plus pyrene (Flu/(Flu+Pyr)), phenanthrene to phenanthrene plus anthracene (Phe/(Phe+Ant)), indeno(1,2,3-cd)pyrene to indeno(1,2,3-cd)pyrene plus benzo(ghi)perylene (IcdP/(IcdP+BghiP)), benzo(ghi)perylene to benzo(a)pyrene (BghiP/BaP) and benzofluoranthenes to benzo(ghi)perylene (BFs/ BghiP)) are listed and compared with those of other sources in Table 6.1. The Phe/(Phe+Ant) and Flu/(Flu+Pyr) ratios were close to the values found in samples of smoke produced by burning six natural

vegetations, such as monsoon evergreen broad-leaf trees and shrubs, from South China (Wang et al., 2009).

Table 6.1 Comparisons of major PAH diagnostic ratios for different sources.

		Flu/(Flu+Pyr)	Phe/(Phe+Ant)	IcdP/(BghiP+IcdP)	BghiP/BaP	BFs/BghiP
This study	$PM_{2.5}$	0.60 ± 0.07	0.75 ± 0.07	0.75 ± 0.06	0.86 ± 0.44	3.98 ± 2.19
	$PM_{2.5-10}$	0.56±0.25	0.85 ± 0.02	0.74 ± 0.01	0.82 ± 0.13	5.21 ± 0.54
Broad-leaf trees	Wang et al. (2009)	0.50-0.55	0.70-0.83	-	-	-
Shrubs	Wang et al. (2009)	0.54-0.60	0.71-0.76	-	-	-
Grasses	Oros et al. (2006)	0.53-0.63	0.70-0.84	-	-	-
Noncatalyst-equipped automobiles	Rogge et al. (1993)	0.61	0.77	0.04	3.34	0.58
Catalyst-equipped automobiles	Rogge et al. (1993)	0.44	0.89	0.09	2.47	1.16
Heavy duty diesel trucks	Rogge et al. (1993)	0.37	0.88	-	1.23	3.5
Chinese cooking	He et al. (2004)	0.36-0.44	0.96	0.19	7.95	0.58
Cereal straw	Hays et al. (2005)	0.50-0.53	-	0.52-1.0	-	-

In general, the diagnostic ratios can be easily differentiated from those of other combustion sources.

The fine aerosol samples also comprised heteroatomic PAH, such as carbazole and 2-methylcarbazole. Pyrolysis of the constituents in biofuels is a likely formation pathway for these compounds. Several nitrogen-containing heterocyclic compounds have been quantified by thermal extraction-two-dimensional GC-MS with heart-cutting in rice straw burning aerosols, representing roughly 7.1 mg g^{-1} of PM (Ma and Hays, 2008). It should be noted, however, that many heterocyclic-PAH may have been unidentified in our study, because of the constrained GC column capacity and the limited molecular selectivity of the MS detector for this type of compounds.

A homologous series of alkyl nitriles (cyanides) from tetradecanenitrile to nonadecanenitrile were detected, but only in fine particles, contributing up to 118 μg g^{-1} OC. It has been proposed that fatty acids react with ammonia during biomass burning or combustion to produce nitriles, which can be applied as useful biomarker tracers (Simoneit et al., 2003).

A series of *n*-alkanals varying from tetradecanal to triacontanal, with an odd carbon number predominance and maximum at C_{23}, were present in the $PM_{2.5}$ smoke particles. These carbonyl compounds represented about 0.05% of the OC mass. A limited number of homologs with minor amounts occur in coarse particles. The *n*-alka-2-ones ranged from

C_{12} to C_{29}, with a maximum at C_{27}, representing 0.11 and 0.07% of the OC mass in fine and coarse particles, respectively. It has been suggested that straight chain ketones are essentially originated from the partial combustion of aliphatic precursors (Oros and Simoneit, 2001b). The isoprenoid ketone 6,10,14-trimethyl-2-pentadecanone was detected in concentrations from 225 to 2176 ng m^{-3} in $PM_{2.5}$, which corresponds to an average contribution of 772 µg g^{-1} OC. Its concentrations in $PM_{2.5-10}$ were much lower (19–43 ng m^{-3}). This isoprenoid constituent has been previously identified as an aerosol component in samples impacted by a coniferous forest fire in Boulder, Colorado (Veltkamp et al., 1996). However, its utilisation as biogenic tracer is questionable, in view of the fact that this branched ketone may be also a partially oxidised product derived from car exhausts (Simoneit, 1986).

Normal even carbon numbered C_{18}-C_{30} alkanols, with C_{22} and C_{24} as the dominant homologs, were detected in smoke samples. These alcohols were present in the epicuticular waxes on plant leaves (Oros and Simoneit, 2001b). They made up about 0.6 and 1.1% of the OC bulk in $PM_{2.5}$ and $PM_{2.5-10}$, respectively.

A series of *n*-alkanoic acid methyl esters ranging from C_{12} to C_{26}, with an even carbon number predominance, have been detected with global concentrations up to 466 ng m^{-3} and 128 ng m^{-3}, which correspond to 496 µg g^{-1} OC and 1223 µg g^{-1} OC in $PM_{2.5}$ and $PM_{2.5-10}$, respectively. Fine et al. (2004) have detected methyl alkanoates from C_{17} to C_{27} in $PM_{2.5}$ emissions from residential wood combustion.

A series of *n*-alkanoic acids, ranging from C_8 to C_{28}, has been detected in the smoke samples. Average CPI values of 9.46 and 5.65 for fine and coarse particles, respectively, reflect the strong even-to-odd carbon number predominance currently associated with vegetative detritus. These compounds are basic units of plant fats, oils and phospholipids (Oros and Simoneit, 2001b; Wang et al., 2009). On average, they represented 1.9 and 2.8% of the OC mass in $PM_{2.5}$ and $PM_{2.5-10}$, respectively. Many saturated dicarboxylic acids were also present in the smoke particles, including the C_3-C_{10} homologs and the hexadecanedioic acid. In accordance with results for fine particle emission from the wood stove combustion of prevalent United States tree species (Fine et al., 2004), nonanedioic acid was found as the major alkanedioic acid. A series of *n*-alkanedioic acids ranging from C_4 to C_{10} have also been detected by Hays et al. (2002) in fine particles from burning of foliar fuels. Furthermore, butanedioic to decanedioic diacids, maximising at C_4 and C_9,

were measured in the emissions of prescribed burnings conducted at two pine dominated forest areas in Georgia, USA (Lee et al., 2005). The utility of low vapour pressure particle-phase dicarboxylic acids as atmospheric tracers of source emissions is doubtful because they can be formed as secondary organic aerosols by oxidation or emitted from motor exhausts (Legrand et al., 2007). On the other hand, high molecular weight alkanedioic acids ($>C_{10}$) have been pointed out as possible oxidation products of hydroxyalkanoic acids from vegetation polyester biopolymer (Oros and Simoneit, 2001b).

Unsaturated and polyunsaturated fatty acids are important components of plant oils (Lísa et al., 2009). Among these, oleic and linoleic acids were present in the smoke samples, representing 0.18 and 0.33% of the organic carbon mass in $PM_{2.5}$ and $PM_{2.5-10}$, respectively.

6.3.3 Biomarkers and other pyrolysis products

In addition to the simple saturated and unsaturated aliphatic acids or diacids, a number of hydroxy-, oxo- and aromatic acids were found in the samples (Figure 6.3), which have almost all been observed in biomass burning aerosols previously (Graham et al., 2002). One of these acids was the glycolic acid (or hydroxyacetic), which has been described as a product of hemicellulose hydrolysis (Girisuta, 2007). Another acid present in the smoke samples was levulinic acid, also known as 4-oxopentanoic acid or γ-ketovaleric acid. It may derive from 5-hydroxymethyl-2-furaldehyde, an intermediate product of the hemicellulose or cellulose hydrolysis (Girisuta, 2007). A series of aromatic acids were consistently found in the samples: benzoic acid, ferulic acid, phthalic acid, cinnamic acid, 4-hydroxybenzoic acid, syringic acid, vanillic acid and sinapic acid. Their most probable source is the combustion of lignin or suberin, though functionalised aromatic constituents are also known to be formed during the pyrolysis of polysaccharides (Graham et al., 2002). Naturally occurring resin acids were also detected in the smoke. They represent a group of diterpenoid carboxylic acids present mainly in softwoods, which can be directly volatilised during combustion (Simoneit, 2002), and included the isopimaric ($C_{20}H_{30}O_2$) and abietic ($C_{20}H_{30}O_2$) acids. Triterpenoids, such as ursolic acid ($C_{30}H_{48}O_3$), are important biomarker constituents of many higher plants, especially of angiosperms. This last biomarker was one of the most abundant compounds in the smoke samples (Figure 6.3).

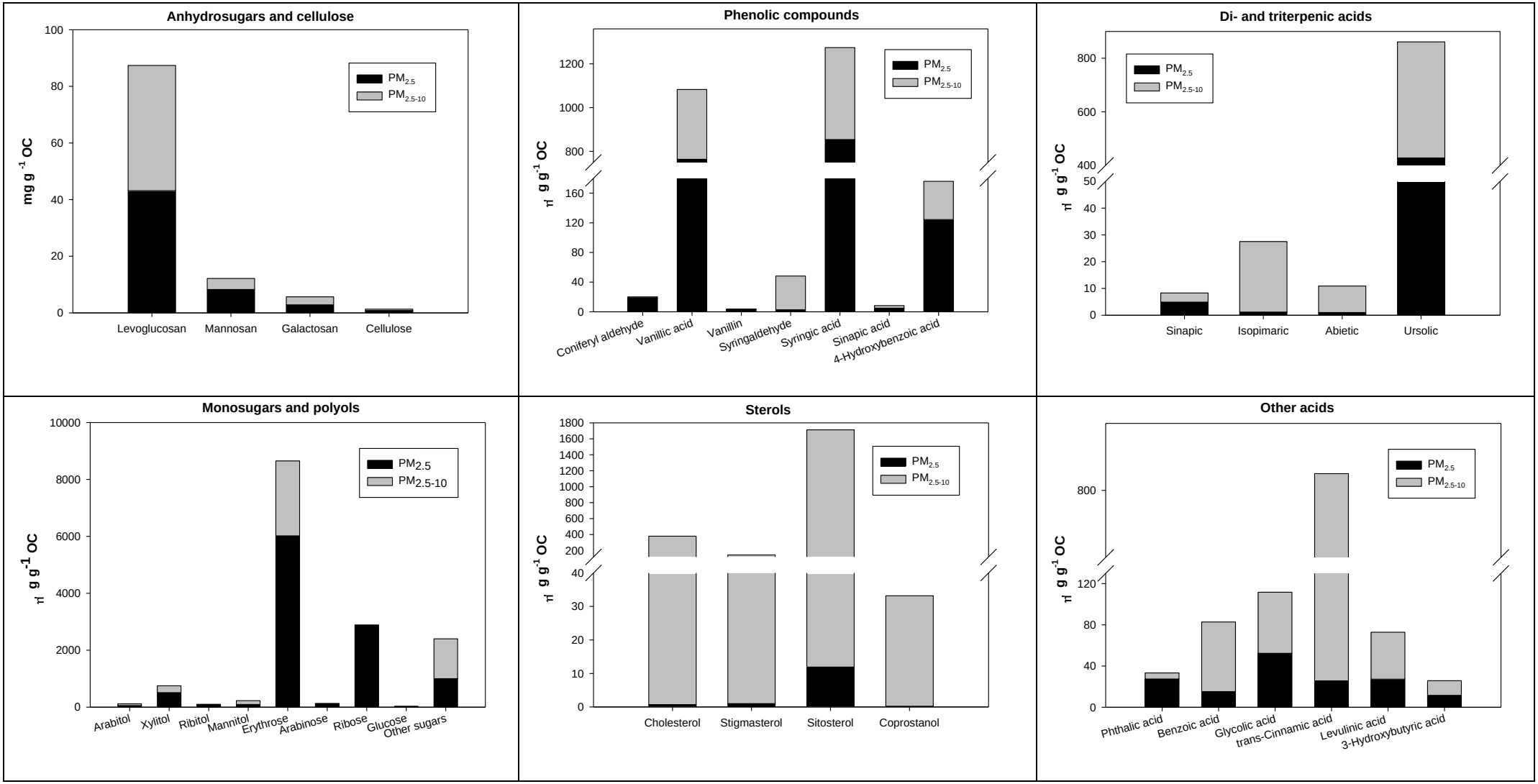


Figure 6.3 Contribution of pyrolysis products and biomarkers to OC in smoke particles (Mannosan and galactosan were quantified using the RRF of levoglucosan; the remaining individual compounds were calibrated using the respective authentic standards).

Methoxyphenols have been identified as prominent lignin thermal degradation products of biofuels and as semi-volatile components of smoke particles (Hawthorne et al., 1988; Kjällstrand et al., 1998). Softwood smoke contains 4-hydroxy-3-methoxyphenyl (guaiacyl or vanillyl) compounds. Hardwood and shrubs give rise mainly to 4-hydroxy-3,5-dimethoxyphenyl (syringyl) compounds because of a different lignin structure (Simoneit, 2002; Wang et al., 2009). Grasses yield essentially 4-hydroxyphenyl (coumaryl) products (Oros et al., 2006). Many different lignin breakdown products have been identified in this study. In all samples, a greater abundance of syringic acid and syringaldehyde compared to vanillic acid and vanillin was observed (Figure 6.3), consistent with the predominance of angiosperms in the forest. Coumaryl-type phenolics (e.g. coumaric acid) were not observed in most samples or were below the detection limit. Some other phenolic compounds were mostly identified in the sample with highest PM concentration, comprising syringyl-type (syringol and methylsyringol), guaiacyl-type (vanillyl methyl ketone, acetovanillone, guaiacol, propioguaiacol, methylguaiacol, ethylguaiacol eugenol, isoeugenol and methoxyeugenol), and benzenediols (catechol, methylcatechol and methoxycatechol). Another benzenediol compound found in fine and coarse smoke samples was hydroquinone (1,4-dihydroxybenzene or 1,4-benzenediol). It was emitted with concentrations of 0.13 μg g^{-1} OC ($PM_{2.5}$) and 0.11 μg g^{-1} OC ($PM_{2.5-10}$). Hydroquinone is considered to be one of the major potential molecular precursors for semiquinone-type radicals in the combustion of complex polymeric and oligomeric structures contained in biomass materials. It is thought to derive from thermal degradation of lignin and other polymeric plant materials that generally contain aryl ether and aryl alcohol linkages (Truong et al., 2008). The presence of hydroquinone in $PM_{2.5-10}$ with a similar enrichment to that in $PM_{2.5}$ is probably due to ejection of quinol-containing particles from the surface of plants and ground (e.g. ash, vegetation detritus, soil, etc.) as a result of the turbulence associated with the very intensive combustion of these fires. A pyrolysis product of hydroquinone, *p*-benzoquinone, was only detected in $PM_{2.5}$. For the most smoke-impacted sample, phenolic compounds represent 0.60% of the fine particle organic carbon content, whilst the contribution to the OC in coarse particles is limited to 0.31%.

Triterpa-*n*,12-dienes, such as 18α(H)-oleana-2,12-diene, 18β(H)-oleana-2,12-diene, and ursana-2,12-diene, represent major pyrolysates of vegetation cuticles found in smoke

samples. These C_{30} pentacyclic triterpenoids were identified by virtue of the molecular ion at *m/z* 408 and characteristic triterpene fragments at *m/z* 189, 203 and 218 (Figure 6.4). A further minor group of two C_{30} pentacyclic triterpadienes was detected, exhibiting characteristic fragment ions resulting from loss of isopropyl from the molecular ion (at *m/z* 365). These compounds are A-neo-triterpa-*m,n*-dienes, such as A-neo-oleana-3(5),12-diene and A-neoursa-3(5),12-diene. Steradienes are steroidal hydrocarbons formed by a sterol dehydration reaction, which is acid catalysed or promoted by elevated temperatures. The principal degradation products have been identified as steradienes or steratrienes resulting from the dehydration of the major plant sterols. Among these, the most representative compounds in the samples were 24-ethylcholesta-3,5-diene, 24-ethylcholesta-3,5,22-triene, 3,5-stigmastadiene and 3,5,22-stigmastatriene. Consistent with the input of vascular plant material, minor amounts of degradation products of both β-sitosterol and stigmasterol (stigmasta-3,5-dien-7-one, stigmast-4-en-3,6-dione and stigmast-4-en-3-one) were also detected in the smoke samples. In addition, four triterpadienes with $C_{30}H_{46}$ formula (m.w. 406), whose individual characterisation was not possible, were also present in all the organic extracts of fine particle samples, with prominent chromatographic areas. As far as we know, these triterpadienes have only been detected in some deciduous tree smoke samples (Oros and Simoneit, 2001b). Associated triterpenoic C_{30} biomarkers, α-amyrin (urs-12-en-3α-ol) and β-amyrin (olean-12-en-3β-ol), with a 2-4-fold higher proportion of the ursene-type compound, were detected in the smoke. These two pentacyclic triterpenes occur naturally in angiosperms, especially in their gums and mucilages (Hays et al., 2002), and are not source specific because they are common in many higher plants. A new ursane-type triterpene, 3-keto-urs-12-ene, was identified in the combustion-particle extracts, standing for 0.62 and 0.12% of the OC-normalised content in $PM_{2.5}$ and $PM_{2.5-10}$, respectively. A pentacyclic triterpenone with the hopene skeleton (A'-Neogammacer-22(29)-en-3-one) was only detected in the fine smoke particles, representing 0.09% of the OC mass. This ketone, also named hop-22(29)-en-3-one or hopenone b, was previously found in the epicuticular waxes of higher plants and in extracts of *Gramineae* species (e.g. Casabuono and Pomilio, 1996), but, as far as we know, this is the first report on its presence in biomass burning aerosols. Together, all these triterpenic and sterol derivative compounds account for 15% of the fine particle OC mass, whereas their contribution in $PM_{2.5-10}$ is around 3%.

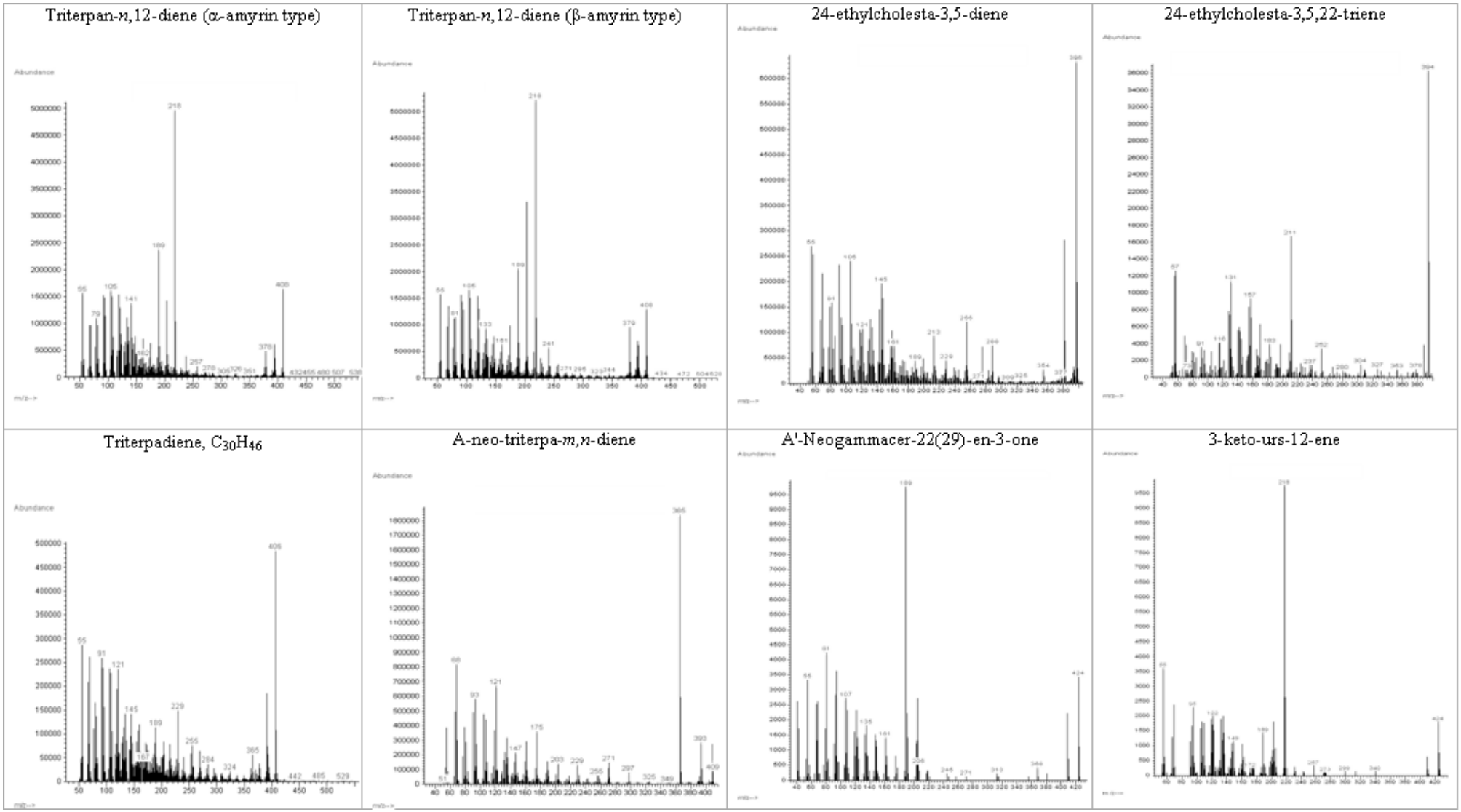


Figure 6.4 Mass spectra of sterol derivatives and triterpenic compounds found in smoke particles.

The quite high total concentration of triterpenoid and sterane structures observed for the $PM_{2.5}$ samples in comparison with similar past biomass burning research may be related to the predominance of angiospermic flora in the shrubland. These compounds are not found in smoke samples from the majority of gymnosperms (Oros and Simoneit. 2001a). On the other hand, different combustion conditions may lead to emissions that vary with fire regime (flaming versus smouldering) and the burn direction/slope (heading versus backing fires). It has been observed that, due to the higher combustion efficiency common to flaming fires, primary organic compounds can decompose to smaller secondary species. The milder combustion conditions characteristic of smouldering fires in addition to an-oxygen rich environment have been shown to produce higher levels of pyrogenic species, specially oxygenated compounds, in spite of some contradictory results in the literature (Engling et al., 2006; and citation therein). Possibly, the burn temperatures during the flaming fires in this study were below those observed during other burning experiments, resulting in higher triterpenoid and steradiene emissions than expected. Moreover, it has been observed that emissions for heading fires, such as those of this study, are significantly higher than emissions for backing fires.

Phytosterols are ubiquitous indicators for the presence of plant-derived material, which is introduced into smoke by volatilisation during burning. The higher concentrations of β-sitosterol relative to that of stigmasterol registered in this study (Figure 6.3) was previously observed for residential fireplace wood smoke (Nolte et al., 2001), particulate matter from deciduous trees subjected to controlled combustion (Oros and Simoneit, 2001b), $PM_{2.5}$ emitted from the combustion of different Bangladeshi biofuels (Sheesley et al., 2003) and aerosols from burning of grasses (Oros et al., 2006). Unlike the majority of earlier wood burning studies, the prescribed burnings in Lousã emitted cholesterol, which has been used as a tracer for assigning meat cooking (Rogge et al., 1991). However, this C_{27} constituent should not be considered as an exclusive tracer for meat cooking emissions, since it was previously detected in pine, oak and eucalypts wood smoke (Nolte et al., 2001). Cholesterol also exists in soil due to the presence and activity of soil microorganisms and higher living organisms (Puglisi et al., 2003). According to Lee et al. (2005), who also detected cholesterol in smoke particles from prescribed fires, its emission process during burning could be similar to steam stripping and vaporisation during meat cooking. A fecal stanol, coprostanol, was found in fine (0.2 µg g^{-1} OC) and coarse (33 µg

g^{-1} OC) smoke particles. The combustion of fecal material of forest animals (e.g. deer) may have contributed to the detection of this biohydrogenation product of cholesterol. In the present study, the average concentrations of α-tocopherol (Vitamin E) represented 180 μg g^{-1} OC and 620 ng g^{-1} OC in coarse and fine particles, respectively. L-Quebrachitol (2-methyl-L-*chiro*-inositol), another vegetation product, was only found in $PM_{2.5-10}$ standing for 0.10% of the OC mass. The vascular plant antioxidant α-tocopherol was identified as a significant component in the smoke from burning bamboo, sugarcane and pampas grass (Oros et al., 2006). It was also found in appreciable amounts in $PM_{2.5}$ emissions from simulated agricultural fires of surface residuals of two major grain crops, rice and wheat (Hays et al., 2005). Among the emissions from the wood stove burning of different hardwood and softwood species, this compound was only detected in the smoke from the combustion of oak (Fine et al., 2004). It was also observed in the smoke from domestic use of different fuels indigenous to South Asia, including coconut leaves, rice straw, dried cow dung patties, briquettes and jackfruit branches (Sheesley et al., 2003).

Other major organic components of smoke particles from biomass burning were monosaccharide derivatives from the breakdown of cellulose. Levoglucosan (L), followed by its stereoisomers [mannosan (M) and galactosan (G)], was the most abundant anhydrosugar measured in the smoke aerosols (Figure 6.3). The relative amounts of the individual anhydrosaccharides in biomass smoke aerosols can be used for further source assignment of specific biofuels (Fabbri et al., 2009, and citations therein). Specifically, the L/M ratio has recently been employed to differentiate the predominance of coniferous versus deciduous wood combustion (Pio et al., 2008). Usual source apportionment methods are appropriate for the assessment of biomass burning contributions in general, but do not enable the estimation of individual inputs from specific biomass burning processes. Thus, the relative anhydrosaccharide composition of smoke particles may elucidate the source contributions from different biofuels or types of combustion (Schmid et al., 2008). The L/M and L/(M+G) ratios obtained in this study (Table 6.2) were close to those reported for softwood, duff, litter and shrub burning, but deviate from values for hardwood, grass or coal combustion. The anhydrosugars presented a two- to ten-fold greater concentration in $PM_{2.5}$ than in $PM_{2.5-10}$. However, the percentages of anhydrosugars in OC do not differ appreciably from the fine to the coarse particulate fractions.

Table 6.2 Ratios of anhydrosugars in emissions from biomass burning (L – levoglucosan, M – mannosan, G – galactosan).

Biomass type	Particle size	L/M	L/(M+G)	Ref.
Shrubland	$PM_{2.5}$	6.3	4.7	This study
	$PM_{2.5-10}$	5.6	3.9	This study
Hardwoods	$PM_{2.5}$	13-24	10.4-14.2	Fine et al. (2004)
	$PM_{2.5}$	13.8-52.3	4.5-39.3	Engling et al. (2006)
	PM_{10}	14.5-14.6	8.5-9.9	Schmidl et al. (2008)
	TSP	4.9-17.3	5.9-20.5	Wang et al. (2009
Softwoods	$PM_{2.5}$	6.9-6.7	2.9-5.0	Fine et al. (2004)
	$PM_{2.5}$	2.6-5.0	2.4-2.8	Engling et al. (2006)
	PM_{10}	3.6-3.9	1.8-2.8	Schmidl et al. (2008)
Lignite	TSP	31-92	31-92	Fabbri et al. (2009)
Grasses	TSP	2.0-33.3	1.7-9.5	Oros et al. (2006)
	$PM_{2.5}$	108-202	54.2-66.1	Engling et al. (2006)
Sage	$PM_{2.5}$	11.1-11.7	6.7-6.9	Engling et al. (2006)
Duff	$PM_{2.5}$	2.4	1.2	Engling et al. (2006)
Green hardwood litter	TSP	4	2	Medeiros and Simoneit (2008)
Green softwood litter	TSP	3.6	2.1	Medeiros and Simoneit (2008)
Charred pine wood	---	2.5	2.0	Otto et al. (2006)
Charred pine cone	---	0.3	0.2	Otto et al. (2006)
Pine needles	$PM_{2.5}$	3.7-6.5	2.3-3.8	Engling et al. (2006)
Shrubs	TSP	1.4-2.2	3.7-4.8	Wang et al. (2009)

The average L/OC ratio of 43 mg g^{-1} OC obtained in this study for $PM_{2.5}$ falls in the range of values reported for other field research. A L/OC ratio of 12.3 mg g^{-1} has been measured for the dry season aerosol in Rondonia (Graham et al., 2003), whereas a ratio of 193 mg g^{-1} has been measured in the same Brazilian region during the wet season (Zdrahal et al., 2002). Lee et al. (2005) obtained a ratio of 10.5 mg g^{-1} for a prescribed pine forest fire in southeast USA. It should be noted that substantial variation in levoglucosan emissions within fuel types and combustion conditions may occur. Thus, specific ratios should be determined to provide correct source apportionment estimates.

Besides anhydrosugars, other sugar compounds positively identified and detected in smoke samples included four polyols (arabitol, xylitol, ribitol and mannitol), four monosaccharides (erythrose, arabinose, ribose and glucose) and the polysaccharide cellulose (Figure 6.3). Many of these sugar compounds have been previously detected in

smoke-impacted samples from the Howland Experimental Forest, Maine (Medeiros et al., 2006), Amazonia (Graham et al., 2002) and a rural Portuguese site (Pio et al., 2008). Schmidl et al. (2008) found sugar alcohols (e.g. arabitol) in notable concentrations in leaf burning samples, which were much higher than in log combustion, suggesting the use of polyols to identify the contribution of leaf burning on high organic matter levels in ambient air. It is possible that many of these monosugar and polyol constituents are primary products of combustion formed either through direct volatilisation from vegetation material or as products of the breakdown of polysaccharides. Some of the sugars may also be formed by hydrolysis of the analogous anhydrosugars under the acidic atmospheric conditions produced by biomass burning (Graham et al., 2002). For those monosaccharides and polyols that appeared simultaneously in both size fractions, concentrations were four- to eighty-fold higher in $PM_{2.5}$ than in $PM_{2.5-10}$. Arabinose and ribose were only detected in fine particles. A clear enrichment in $PM_{2.5}$ samples and moderate correlations with levoglucosan (r^2=0.3–0.8) suggest a dominant combustion source for these compounds. A further, non-dominant, source for these sugar constituents may be suspended biogenic detritus, such as plant material, bacteria, fungi, spores, etc. (Graham et al., 2002).

6.4 Conclusions

This work reports the detailed organic composition of smoke particles from prescribed burnings in a shrub-dominated forest. Novel organic tracer signatures for emissions from biomass burning were obtained. The data set indicates that approximately 50% of the particulate mass is carbonaceous in nature with a clear dominance of organic carbon. The OC concentrations were 46-fold higher in $PM_{2.5}$ than in $PM_{2.5-10}$. The major fraction of the extractable and chromatographically resolved organic matter was composed by triterpenoids with the oleanane and ursane skeletons, steradienes and steratrienes, including unaltered biological precursors (biomolecules) and their degradation products (pyrolysates). These compounds account for 15 and 3% of the OC mass in $PM_{2.5}$ and $PM_{2.5-10}$, respectively. Aliphatic lipids (*n*-alkanoic acids, *n*-alkenoic acids, *n*-alkanols and *n*-alkanes), and anhydrosugars (levoglucosan and its stereoisomers) constituted another large fraction of OC. Consistent with the predominance of angiosperms in the forest, syringyl-type phenols from lignin pyrolysis were emitted in higher proportion than guaiacyl-type phenols. Polycyclic aromatic hydrocarbons were also present as minor

constituents. The PAH molecular diagnostic ratios in this study are different from other combustion sources such as cooking, catalyst-equipped automobile engine exhaust and heavy-duty diesel truck engine exhaust. Hence, these ratios may be taken as indicative of vegetation burning in source apportionment studies. The average concentration of 43 mg of levoglucosan/g of OC in the emitted fine particles falls in the wide range of values reported in the literature for biomass burning aerosols. The levoglucosan/OC relationships for deriving the amount of OC from biomass combustion in ambient aerosols should be taken with prudence. Since the ratios are quite variable for different burning conditions and wood types, it has yet to be estimated more specific emission factors with application to wildfires under heat wave conditions in Mediterranean forests.

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CHAPTER 7

Chapter 7. Smoke emissions from biomass burning in a Mediterranean shrubland

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Abstract

Gaseous and particulate samples from the smoke from prescribed burnings of a shrub-dominated forest with some pine trees in Lousã Mountain, Portugal, in May 2008, have been collected. From the gas phase Fourier transform infrared (FTIR) measurements, an average modified combustion efficiency of 0.99 was obtained, suggesting a very strong predominance of flaming combustion. Gaseous compounds whose emissions are promoted in fresh plumes and during the flaming burning phase, such as CO_2, acetylene and propene, produced emission factors higher than those proposed for savannah and tropical forest fires. Emission factors of species that are favoured by the smouldering phase (e.g. CO and CH_4) were below the values reported in the literature for biomass burning in other ecosystems. The chemical composition of fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) particles was achieved using ion chromatography (water-soluble ions), instrumental neutron activation analysis (trace elements) and a thermal-optical transmission technique (organic carbon and elemental carbon). Approximately 50% of the particulate mass was carbonaceous in nature with a clear dominance of organic carbon. The organic carbon-to-elemental carbon ratios up to 300, or even higher, measured in the present study largely exceeded those reported for fires in savannah and tropical forests. More than 30 trace elements and ions have been determined in smoke aerosols, representing in total an average contribution of about 7% to the PM_{10} mass.

Keywords: Forest fires, greenhouse gas emissions, particulate emissions, organic and elemental carbon, chemical elements, water soluble ions.

7.1 Introduction

Researchers estimate that from 1850 to 1980 between 90×10^{15} and 120×10^{15} Pg of carbon dioxide (CO_2) were emitted to the atmosphere from forest fires in the tropics (NASA, 2009). In comparison, during the same time interval, the burning of coal, oil, and gas in industrialised countries contributed to the release of 165×10^{15} Pg of this greenhouse gas (NASA, 2009). Nowadays, an estimated 5.6 Pg of carbon are annually released into the atmosphere due to fossil fuel burning, whereas fires in tropical forests contribute another 2.4 Pg of carbon, i.e. about 40% of the total (NASA, 2009). Over the last decades, the amount of biomass burning has expanded worldwide. In particular, summer heat-waves in southern Europe are forecast to increase even more in frequency in association with projected climate change as a result of global warming, and hence the number and severity of wildfires is expected to increase in the future. In the past 25 years, the total number of fires reported has risen sharply from around 20,000 yr^{-1} to 60,000 yr^{-1} in the five Mediterranean Member States of EU15 - France, Greece, Italy, Portugal and Spain (EEA, 2006).

Besides CO_2, biomass burning results in the release into the atmosphere of significant quantities of other chemically active products. Emissions of carbon monoxide (CO) and methane (CH_4) perturb the atmospheric oxidation efficiency by reacting with hydroxyl radicals (Crutzen and Andreae, 1990). Just as in urban areas, emissions of nitric oxides (NO_x) and hydrocarbons react to form ozone, leading to higher concentrations in the tropics than in other regions due to the stronger impact of biomass burning (Thompson et al., 2001). On the other hand, smoke particles degrade visibility, could affect health and have highly uncertain impacts on climate forcing (Spracklen et al., 2007).

Current global estimates of gas and particulate emissions from biomass burning are largely varying (Ito et al., 2004; Jain et al., 2006; NASA, 2009; Randerson et al., 2006; Schultz et al., 2008; van der Werf et al., 2004): 220-13,500 Tg CO_2 yr^{-1}, 120-680 Tg CO yr^{-1}, 11-53 Tg CH_4 yr^{-1}, and 2-21 Tg NO_x yr^{-1}. Annual estimates of particulate matter smaller than 2.5 μm in diameter ($PM_{2.5}$) produced by biomass burning are around 38 Tg (NASA, 2009; Randerson et al., 2006).

The scientific community is placing greater emphasis on assessing more accurately the emissions from biomass burning and on estimating its environmental impacts. Some studies focused on the characterisation of distinct types of biomass fires in savannahs and tropical forests have been recently performed (Andreae and Merlet, 2001; Koppmann et al., 2005; Neto et al., 2009; Reid et al., 2005; and references therein). However, most of these studies are exclusively based on gaseous measurements and, as far as we know, none of them concern the Mediterranean area. It is known that emissions depend wholly on the forest fuel types, combustion process, and weather conditions (Pio et al, 2008), and that emission factors are required for modelling atmospheric processes, inventories, and source apportionment studies. Thus, it is desirable to ascertain more precise emission factors reflecting country and regional conditions. The aim of this research is to obtain a detailed characterisation of smoke emissions from a Mediterranean shrubland.

7.2 Experimental

7.2.1 Sampling details

A series of experimental fires have been conducted at a shrub-dominated forest in Lousã Mountain (~ 40º04'38''N and 08º09'35''W), central Portugal, in May 2008. Since these fires have been applied in a knowledgeable manner under selected weather conditions to accomplished predetermined research objectives, the chemical composition of their emissions may differ appreciably from wildfires. During the prescribed burns, the temperature and relative humidity were in the ranges 18–21ºC and 16–59%, respectively, conditions which are far less severe than those registered during heat wave triggered wildfires in summer. Summer wilfires occur, in particular, when the atmospheric circulation forms an important ridge associated with south-easterly flow, and a strong advection of very hot (T>30°C) and dry air from northern Africa that is additionally heated when passing over central Iberia (Pio et al., 2008).

The fuel characterisation was based on a combination of destructive and non destructive methods. To determine the fuel load and fuel bulk density, destructive sampling was used. From this basic information, specific allometric relationships between height and fuel load/bulk density could be obtained. Micro plots of 0.25 m^2 and 1.0 m^2 were established for destructive sampling of the dominant shrubs. The linear intersect method

was used for determining the percent cover, height and bio-volume. In order to look over probable vegetation distribution gradients along each plot length, transects were established. Linear measurements were made on the interception of the vegetation through which the vertical plane of the line passed. These gave information on cover of shrub species and composition of the fuel complex. The height/length measurements were used to estimate the shrub loads. The fuel moisture content was obtained by drying fuel samples in an oven at 105ºC for 24 h. The vegetation cover was composed by some isolated pine trees (*Pinus pinaster*) and a continuous mass of dwarf Spanish heath (*Erica umbellata*), Spanish heather (*Erica australis*) and prickled broom (*Chamaespartium tridentatum*). On average, the moisture content of these shrubs was 40.7%, 48.7% and 45.6%, respectively. The three dominant vegetation species represented 16%, 43% and 32% of the fuel cover, correspondingly, presenting heights between 54 and 104 cm. The remainder percentage of fuel cover corresponded to parched vegetation composed of *Erica* species and *Chamaespartium tridentatum* with moisture contents of about 7.9% and 5.7%, respectively. Taking into account the vegetation abundance and the individual moisture content of the plant species, a 43.7% moisture content average was obtained for the shrubland. From the allometric measurements, a fuel bulk density of 2.7 kg m^{-3} was achieved. The fuel load was estimated to be 27.7 ton ha^{-1} in a wet-weight basis, which corresponds to 15.6 ton ha^{-1} in a dry-weight basis.

A total of seven plots were burned. Each compartment was ignited by hand from its surrounding firebreak roads using a drip torch. During these prescribed fires, a tripod high-volume sampler (Tisch Environmental Inc.) with impaction plates operating at a flow of 1.13 m^3 min^{-1} was used to collect sequentially, on pre-baked quartz fibre filters, coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$) smoke particles. The impaction system for capturing PM_{10} was designed in accordance with the Marple and Rubow's theory (1986) and constructed in a local metal-mechanic industry. In parallel, Tedlar bags previously flushed with N_2 have been used for the collection of gas samples. Pre-removal of water vapour from the air stream was carried out in a U glass tube filled with glass spheres, immersed in an ice bath. In addition, and previously to the water vapour removal, the air stream was filtered through a 4.7 mm quartz filter to remove particles before passing to the collection system, which also contained a Teflon-lined diaphragm pump connected to a needle valve and a calibrated rotametre operating at a flow rate of 1 L min^{-1}. One of the Tedlar bags has been

sampled in the same location prior to the fires aiming to obtain background levels. After sampling, the bags were stored in opaque containers in order to minimise U.V. radiation of the samples. The time period between sampling and analysis was reduced to a few hours to avoid secondary reactions.

7.2.2 Chemical analysis

All gas phase samples were examined for CO_2, CO, N_2O, NO, NO_2, SO_2, NH_3, CH_4, ethane (C_2H_6), propene (C_3H_6), acetylene (C_2H_2) and methanol (CH_3OH) using a Gasmet™ Dx – 4000 multicomponent analyser. This equipment includes a high-resolution Fourier transform infrared (FTIR) spectrometer, a 0.4 L rhodium coated aluminium sample cell with a fixed absorption path length of 5.0 m, and a Peltier cooled mercury-cadmium-telluride (MCT) detector with a scan frequency of 10 s^{-1} and a wavenumber range of 900-4200 cm^{-1}. The Gasmet™ Dx 4000 has an accuracy of ±2%. The instrument allows simple calibration using only single component calibration gases. It operates with the CALCMET analysis software, which gives access to a reference library.

It should be noted that there is a possibility that compounds such as methanol, SO_2 and NH_3 might have been trapped, at least partially, in the water condenser chiller of the air sampling system. In addition, compound losses due to a combination of adsorption to and diffusion through the bag walls might also have occurred. In fact, decline in concentration levels of several classes of volatile compounds with bag storage time have been observed in some researches (Beauchamp et al., 2008; Trabue et al., 2006; Wang et al., 1996). Measured concentrations for gaseous species represent, therefore, a lower limit of the true atmospheric values.

The carbonaceous content of particulate matter was analysed by a thermal–optical transmission technique (Carvalho et al., 2006). To avoid the potential interference of carbonates from soil with the signal of EC and OC, the filter samples were subjected to a pretreatment in HCl vapour. For the determination of soluble inorganic ions, small parts of the filters were extracted with ultra pure Milli-Q water. Dionex AS14 and CS12 chromatographic columns with Dionex AG14 and CG12 guard columns coupled to Dionex AMMS II and Dionex CMMS III suppressors, respectively for anions and cations, have been used. The trace metal speciation has been performed by Inducted Neutron Activation Analysis (INAA). Filter punches were rolled up and put into a thin foil of aluminium and

irradiated for 7 h at a thermal neutron flux of 1.2×10^{13} cm^{-2} s^{-1} in the Portuguese Research Reactor. After irradiation, the samples were removed from the aluminium foil and transferred to a polyethylene container. For each irradiated sample, two gamma spectra were measured with hyperpure germanium detectors, one spectrum 2–3 days after irradiation and the other one after 4 weeks. The k_0 method was used and 1 mm diameter wires of 0.1% Au–Al were co-irradiated as comparators.

7.2.3 Calculations

The emission factor (EF) is a parameter that relates the emission of a particular species of interest to the amount of fuel burned. It is defined as the amount of a compound released per amount of dry fuel consumed, expressed in units of g kg^{-1}. The carbon combusted in a fire is emitted into the measurable portions of a smoke plume in five forms of carbon: CO_2, CO, CH_4, non-methane hydrocarbons (NMHC), and particulate carbon (PC). The emission factor of a species, *n*, is then obtained from the ratio of the mass concentration of that species to the total carbon concentration emitted in the plume. Thus, the emission factor is expressed in units of mass of species *n* emitted per unit mass of carbon burned. To convert this emission factor to the more frequently used grams of *n* produced per kg of dry matter burned, the previous ratio is multiplied by the mass fraction of carbon in the fuel (Reid et al., 2005):

$$EF_n = \frac{[n]}{[CO_2] + [CO] + [CH_4] + [NMHC] + [PC]} \times \%C_{fuel} \quad (1)$$

It has been estimated that the dominant shrub species in the Portuguese forest have a mean carbon content of 48% (Silva et al., 2008). It should be also noted that background levels have been subtracted from measurements in the smoke plumes. The term [NMHC] in the equation was considered to be the sum of ethane, propene, acetylene and methanol. These species are among the dominant volatile hydrocarbons emitted by fires. On the other hand, total emissions of NMHC accounted for 1-2%, or less, of fuel C burned, while CO_2 and CO comprise 87-92% (Urbanski et al., 2009). Thus, the error committed in the calculation of individual emission factors by taking just a few NMHC species appears to be negligible.

To evaluate the completeness of combustion, it can be considered that >90% of the carbon combusted in a fire is emitted in the form of CO_2 and CO, and <10% of carbon is in species such as hydrocarbons and particulate carbon. Keeping this in mind, the modified combustion efficiency (MCE) is calculated as follows:

$$MCE = \frac{[CO_2]}{[CO_2] + [CO]} \quad (2)$$

A MCE > 90% suggests that more than 50% of the emissions were produced by flaming combustion, whereas when MCE < 90%, more than 50% of the emissions were originated by smouldering combustion (Ward and Hardy, 1991).

7.3 Results and Discussion

7.3.1 Gaseous species

The MCE, i.e. the ratio of the carbon released as CO_2 to the sum of the carbon released in the form of CO_2 and CO, was 0.99±0.01, indicating fires typically in the flaming phase. Among other factors, the low degree of fuel packing may have contributed to such a high MCE values (Neto et al., 2009). The EFs resulting from the samples collected during the prescribed burns are presented in Figure 7.1. In general, EFs are strongly dependent on MCE. Figure 7.2 depicts the correlation between EFs and MCE for CO_2, CO, and CH_4. The slope of the regressions indicates the importance of the burning phase (flaming versus smouldering) in estimating the emission factors, i.e., the steeper the slope, the larger the dependence on the type of combustion (Sinha et al., 2003). Positive slopes point out that emissions are promoted by flaming combustion, whereas negative values suggest that emission of the species is favoured by the smouldering phase.

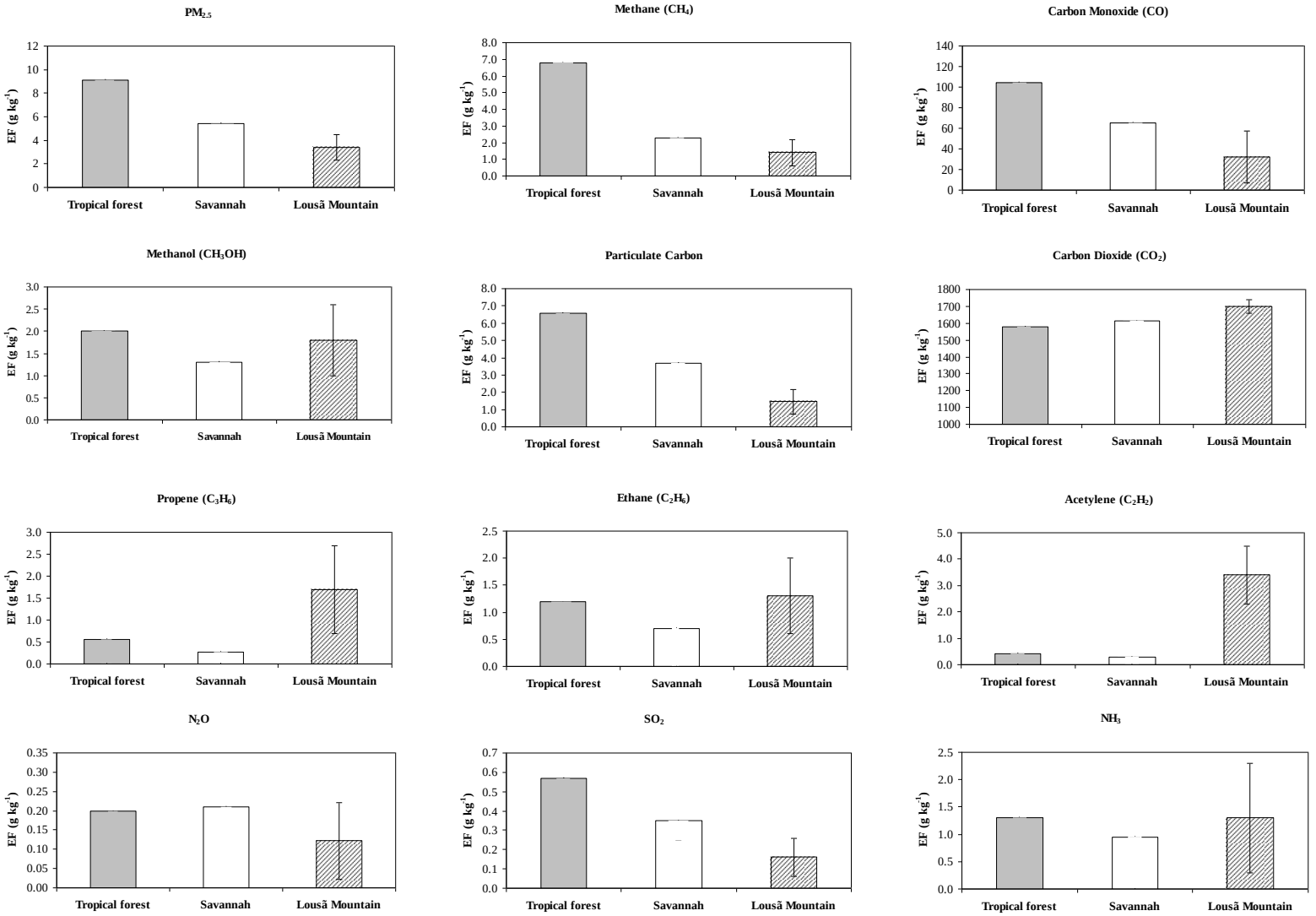

Figure 7.1 Comparison of emission factors (given in gram species per kilogram dry matter burned, mean ± standard deviation) for pyrogenic species. Data source for savannah and tropical forest is Andreae and Merlet (2001).

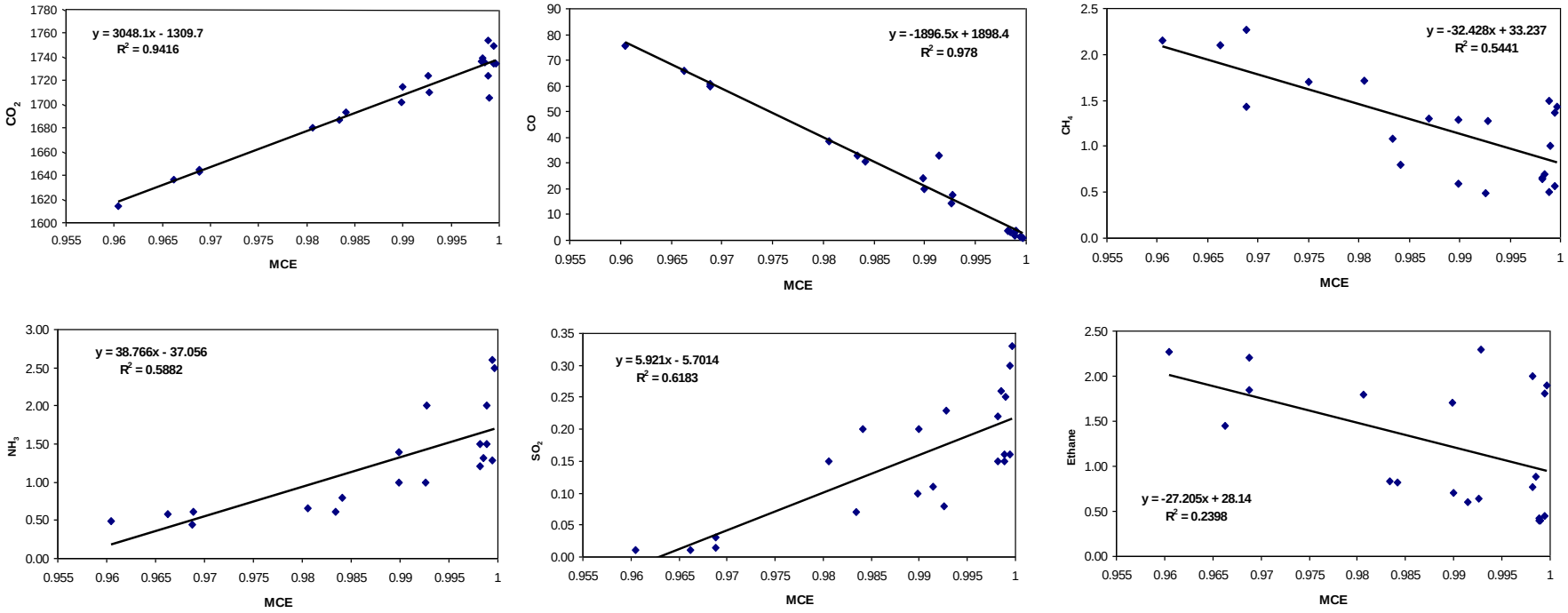

Figure 7.2 Correlation between EF (g kg^{-1}, dry basis) of some gaseous species and MCE.

The EF_{CO_2} obtained for Lousã Mountain are higher than those proposed by Andreae and Merlet (2001) for savannah and tropical forest fires. However, measurements of smoke emissions with high combustion efficiency in grassland and woodland savannah ecosystems in South Africa and Zambia provided average EF_{CO_2} of 1701 g kg^{-1} (Ward et al., 1996). Neto et al. (2009) reported EF_{CO_2} of 1631–1625 g kg^{-1} (ignition), 1690–1741 g kg^{-1} (flaming) and 1540–1548 g kg^{-1} (smouldering) for an Amazonian forest clearing fire. McMeeking et al. (2009) obtained average EF_{CO_2} of 1552±150 g kg^{-1} (MCE=0.915±0.033), 1489±176 g kg^{-1} (MCE=0.905±0.043), 1538±125 g kg^{-1} (MCE=0.909±0.029), 1632±150 g kg^{-1} (MCE=0.930±0.029) and 1311±325 g kg^{-1} (MCE=0.917±0.068), from a series of laboratory burns of fuels from montane, rangeland, chaparral, coastal plain and boreal forest, respectively, reflecting the different contributions from flaming and smouldering combustion.

The combination of lower particulate matter EFs and higher CO_2 EFs indicates that the prescribed fires exhibited more efficient combustion than wildfires or slash reduction burns. This is likely due to more efficient burning of fine fuels under prescription conditions, which minimises consumption of soil organic layers and smouldering of heavy fuels. Combustion of these fuel components often results in higher emission of products of incomplete combustion (Mickler et al., 2007). Taking into account a fuel load of 15.6 ton ha^{-1}, the experiment of this study provided an average emission rate of CO_2 of 26 ton ha^{-1}, which means that 89% of the carbon content of biofuels was emitted to the atmosphere in the form of carbon dioxide.

As expected, contrarily to the results obtained for CO_2, EF_{CO} in this study fall below reported values for fires in other ecosystems. Hegg et al. (1990) and Laursen et al. (1992) obtained EF_{CO} values between 34 and 175 g kg^{-1} (average of 95±16 g kg^{-1}). For diverse fires in North America. Yokelson et al. (2009) reported values of 75±26 g kg^{-1} and 83±14 g kg^{-1} for crop residues and deforestation fires, respectively. Bertschi et al. (2003) measured EF_{CO} from 128 to 165 g kg^{-1} in residual smouldering combustion (RSC) in a series of laboratory fires and in a wooded savannah (miombo). The authors concluded that EFs for RSC-prone fuels, including downed logs, duff, and organic soils, from the boreal forest and wooded savannah are very different from the EFs for the same compounds measured in fire convection columns above these ecosystems. The EF_{RSC} for CO raised by a factor of 2.1 when comparing lofted emissions with RSC. Very high-intensity flaming

combustion, such as that observed in Lousã Mountain, leads to more complete combustion and correspondingly lower proportions of incompletely oxidised combustion products like carbon monoxide.

Methane emission factors reported from the few existing studies differ by a factor of 20, varying from 1 to 23 g kg^{-1}, with higher values for smouldering combustion (Bertschi et al., 2003; Ferek et al., 1998; Radojevic, 2003). In fact, methane emissions are much higher for fires with low combustion efficiency (Koppmann et al., 2005). Ward et al. (1991) reported EF_{CH_4} of 1.0–1.6 g kg^{-1} for flaming-phase cerrado fires, whereas values up to 10.8 g kg^{-1} have been obtained for smouldering combustion in primary forest slash in Brazil. Neto et al. (2009) obtained EF_{CH_4} of 3.4 and 13.1 g kg^{-1} in an Amazonian forest clearing fire during the flaming and smouldering phases, respectively. The EF_{CH_4} obtained in this study is in the range of 0.9–5.6 g kg^{-1} measured over real biomass fires in the United States (Hegg et al., 1990). The contribution of CH_4 as a greenhouse gas is 21 times that of CO_2 (Barker et al., 2007). Multiplying the average EF_{CH_4} of 1.4 g kg^{-1} by this number, the emission factor for CO_2 equivalent to the emitted CH_4 is 29.4 g kg^{-1}, which represents only 2% of the 1700 g kg^{-1} released originally as CO_2.

Emission factors of both NO and NO_2 in this study were always less than 0.3 g kg^{-1}, which are far below the average EF_{NO_x} (as NO) of 3.9 and 1.6 g kg^{-1} published by Andreae and Merlet (2001) for savannah/grassland and tropical forest burning, respectively. Since most of the NO_x in smoke comes from nitrogen compounds in the biomass itself (Radojevic, 2003), the differences in EFs may be due to variations in the N content of biofuels burned. In fact, while the nitrogen content in trees of Amazonia was estimated to be in the range 1.3–3.2% (Parolin et al., 2002), the dominant shrub species of the Portuguese forest have a content lower than 0.8% (Silva et al., 2008). A reduction of 25% has been observed in the nitrogen content after rainfall events (Silva et al., 2008). Given that some precipitation had been registered a few days before the biomass burning experiments, it is likely that some nitrogen leaching has occurred. However, the drawbacks associated with a possible loss of compounds during sampling must also be pointed out to explain the low EF_{NO_x} values. For NH_3, the shrub-dominated ecosystem emission factors are close to what has been measured for other temperate woods, savannah and tropical forest (Andreae and Merlet, 2001; Yokelson et al., 2007).

The EFs calculated in this study for acetylene, ethane and propene are weakly correlated with MCE, suggesting that these emissions do not present a strong dependence on the combustion process. The EF estimates show significant departure from the values quoted by Andreae and Merlet (2001) for tropical forest and savannah fires. According to Yokelson et al. (2003), many reactive initial emissions may be depleted in aged smoke, lowering the corresponding emission factors. Thus, the high values obtained for VOC species in Lousã Mountain may be associated with the very fresh nature of the smoke plumes. It must be also pointed out that VOC emission factors presented higher values for boreal forest fires than those obtained for tropical savannahs and tropical forest (Urbanski et al., 2009).

The average EF_{CH_3OH} of 1.8 g kg^{-1} inferred from these measurements is lower than the 2.73 g kg^{-1} emission factor measured in western Canada and Alaska plumes (Rinsland et al., 2007), the 2.0 g kg^{-1} extratropical forest emission factor (Andreae and Merlet, 2001) and the 2.03 g kg^{-1} measured in a large, isolated North Carolina, USA plume (Yokelson et al., 1999). An EF_{CH_3OH} of 1.07 g kg^{-1} has been derived for residual smouldering combustion of boreal fuels from laboratory fire measurements (Bertschi et al., 2003). Goode et al. (2000) reported an emission factor of 1.35 g kg^{-1} from analysis of Alaska biomass burning plumes, which approaches the 1.3 g kg^{-1} proposed for savannah burning (Andrea and Merlet, 2001). However, our EF_{CH_3OH} of 1.8 g kg^{-1} is close to the 1.71 g kg^{-1} reported by Yokelson et al. (1999) by averaging 13 measurements obtained with a wide range of techniques.

Our results for SO_2 show a positive slope for EF versus MCE, in accordance with past studies that have indicated that SO_2 is preferentially released in flaming combustion (e.g. Ferek et al., 1998; Sinha et al., 2003). The scarce EF_{SO_2} found in the literature present a large variability, since, in addition to the dependence of smoke properties on combustion phase, the fuel sulphur content varies greatly (Sinha et al., 2003). Also, the S-containing emissions depend on the partitioning of sulphur among ash, SO_2 in the gas phase and particulate matter.

7.3.2 Particulate matter

The $PM_{2.5}$ and $PM_{2.5-10}$ reached, respectively, concentrations up to 12.5 and 1.14 mg m^{-3} in the smoke plume. In line with other studies (Andreae and Merlet, 2001), $PM_{2.5}$ represented around 80% of the PM_{10} mass. The particulate matter emission factors estimated in this work are generally below those obtained for other smoke plumes with lower combustion efficiencies. For example, $EF_{PM_{2.5}}$ in the range 3.5–16 g kg^{-1} have been obtained in various types of measurements in the Amazonian region (Neto et al., 2009; and references therein). Ward et al. (1991) measured $EF_{PM_{2.5}}$ ranging from 1.5 to 8.0 g kg^{-1} for African savannah ecosystems. It should be noted that particle emission factors depend on the plume dilution. At low levels of dilution, semivolatile species largely occur in the particle phase, but increasing dilution reduces the concentration of semivolatile species, shifting this material to the gas phase in order to maintain phase equilibrium. Under the highly dilute conditions found in the atmosphere, partitioning of the emissions is strongly influenced by the ambient temperature and the background organic aerosol concentration (Donahue et al., 2006; Shrivastava et al., 2006).

Since emission factors of particulate matter are highly variable depending on plume dilution, fuel type and combustion efficiency (Reid et al., 2005), and taking into account differences in sampling and analytical techniques, the mass fractions of OC in biomass burning aerosols published in the few studies available are also very discrepant. The OC particulate content reported for flaming fires range between approximately 37 and 65% (Table 7.1).

Table 7.1 Comparison of carbon measurements of fresh biomass burning smoke (flaming phase). Values for this study are expressed as mean ± standard deviation.

	PM Size	**OC/EC Ratio**	**OC mass fraction of PM (%)**
Savannah (Andreae et al., 1998)	PM_2	4.3	44
Savannah (Cachier et al., 1995)	TSP	8.3	40-66
Cerrado (Ferek et al., 1998)	PM_4	8.3	61±20
Cerrado (Ward et al., 1992)	$PM_{2.5}$	16.7	57
Pasture (Ferek et al., 1998)	PM_4	9.1	66±11
Temperate forest (Ward et al., 1992)	$PM_{2.5}$	10	50
Tropical forest (Ferek et al., 1998)	PM_4	6.7	53±20
This study	$PM_{2.5}$	88±46	50±8
	$PM_{2.5-10}$	128±73	44±11
	PM_{10}	93±23	44±5

For smouldering fires, the OC content published in the literature represents 62±6% of the PM mass (Reid et al., 2005). The mass fraction of EC in smoke particles is even more variable, differing by over a factor of 5 during flaming phase combustion. The carbonaceous fraction of smoke samples from any of the fires in this study was dominated by organic carbon (OC/PC≈97%) and OC/EC ratios much higher than those reported for other biomass burning events. Field and laboratory studies have attributed the high OC production in fire plumes to condensation of large hydrocarbons, enhanced isoprenoid emissions, acid-catalysed reactions and very rapid oxidation of low-volatility organic vapours (Grieshop et al., 2009; and references therein). The combination of all these factors may have contributed to the very high OC/EC ratios observed in the present study. It should be noted that high OC/EC ratios have also been found for atmospheric aerosols collected in a rural location in Portugal during the 2003 summer intense wildfire period (Pio et al., 2008). Differences between values generated by the current investigation and those reported in the literature may also derive from the methodologies used for the analysis of carbon, since an inter-laboratory comparison have shown that the OC/EC absolute split is not yet solved (Schmid et al., 2001). However, results of this international round robin test on the analysis of carbonaceous aerosols positioned the University of Aveiro within the group with "best estimates". In addition, the comparison between the methodology of the University of Aveiro and the "European Supersites for Atmospheric

Aerosol Research" (EUSAAR-2) protocol (Cavalli et al., 2009) for the quantification of the different carbon fractions in atmospheric aerosol samples gave similar results for OC and EC, without significant differences at a 95% confidence level (Nunes et al., 2010).

Taking into account the gravimetric data and all identified aerosol species, it is possible to reconstruct the $PM_{2.5}$ and PM_{10} mass emissions and to infer the organic matter-to-organic carbon (OM/OC) factor. This factor is used to compute the total organic mass concentration, accounting for associated O, H, N, and other elements, from the measured C mass concentrations attributed to OC (McMeeking et al., 2009). The equation used was as follows:

$$PM_{2.5} \text{ or } PM_{10} = \Sigma \text{ ionic species} + \Sigma \text{ metals} + EC + OC \times f \quad (3)$$

where *f* represents the OM/OC ratio. Based on these calculations, average values of 1.9 and 2 have been estimated for the OM/OC ratios in $PM_{2.5}$ and PM_{10}, respectively. In a review of biomass burning emissions, Reid et al. (2005) reported OM/OC factors of 1.4–1.8. Results from a laboratory investigation of organic aerosols from wood fires suggested an OM/OC ratio of about 2 (Grieshop et al., 2009).

The water-soluble species, ranked in order of concentrations, were Na^+, Ca^{2+}, SO_4^{2-}, Cl^-, K^+, NO_3^-, Mg^{2+} and NH_4^+, which globally represent about 4% of the PM_{10} mass (Table 7.2). Excepting for NO_3^-, NH_4^+ and K^+, ionic species in the coarse mode were more enriched than those in the fine mode. It has been reported that the major ionic species were Cl^-, SO_4^{2-}, K^+ and NH_4^+ for savannah fires (Andreae et al., 1998) and SO_4^{2-}, NH_4^+, K^+, NO_3^- and Cl^-, for fires in the Amazon basin (Falkovich et al., 2005). Besides the dependence on burning phase, the observed differences may be explained by the variability in biomass density, elemental composition and moisture content. Contrarily to what was observed by Andreae et al. (1998), in this study, nitrate was predominantly present in the fine aerosol fraction.

Table 7.2 Water-soluble ions (expressed as wt % of particle mass, mean ± standard deviation) obtained in samples from Lousã Mountain and values from the literature.

Water-soluble ions	$PM_{2.5}$ Lousã	$PM_{2.5-10}$ Lousã	PM_2, $PM_{2.5}$ or PM_4 (literature)	Biome type (literature)
Cl^-	0.28±0.20	0.33±0.43	2.3-11	Savannah
			1.7	Grassland
			1.0-6.0	Cerrado
			0.2-1.7	Tropical broadleaf
NO_3^-	0.11±0.10	0.09±0.07	0.33-0.62	Cerrado
			0.12	Tropical broadleaf
SO_4^{2-}	0.32±0.19	0.44±0.14	0.35-0.72	Cerrado
			0.39-0.90	Tropical broadleaf
Na^+	0.18±0.18	0.74±1.15	0.13-0.8	Savannah
			0.1	Grassland
			0.01-1.0	Cerrado
			0.01-0.2	Tropical broadleaf
NH_4^+	0.05±0.05	0.02±0.02	0.05-0.1	Cerrado
			0.06-0.09	Tropical broadleaf
K^+	0.21±0.28	0.16±0.18	1.8-6.2	Savannah
			2.9	Grassland
			1.3-18	Cerrado
			0.4-5.5	Tropical broadleaf
Mg^{2+}	0.06±0.04	0.16±0.10	<0.06-0.6	Savannah
			0.3	Grassland
			0.03-0.5	Cerrado
			0.01-0.6	Tropical broadleaf
Ca^{2+}	0.26±0.06	0.65±0.42	0.0029-2.46	Savannah
			0.7	Grassland
			0.1-12	Cerrado
			0.06-5	Tropical broadleaf
Sum	1.5±0.10%	2.6±0.31%		

bdl – below detection limit

Data sources for savannah are Andreae et al. (1998), Cachier et al. (1995) and Maenhaut et al. (1996).

Data source for grassland is Ferek et al. (1998).

Data sources for cerrado and tropical broadleaf are Ferek et al. (1998), Ward et al. (1991) and Yamasoe et al. (2000).

The difference between results may be due to the somewhat higher age of the savannah fire plumes, which would make additional formation of HNO_3 and its subsequent absorption on mineral aerosol particles. The mass fraction of water-soluble potassium determined in this study is surprisingly lower than values reported for fires in savannah, grassland, cerrado and tropical broadleaf. However, Chen et al. (2007) found highly variable emission factors in laboratory-controlled fires by burning eight wildland fuels. Depending on the biofuel, the mass percentages of potassium were as high as 23.7%, but they were particularly low (<1%) in the smoke of certain grasses and shrubs.

The observed excess of positive ions correlates well with the concentrations of calcium ions (Figure 7.3), suggesting an origin, at least in part, on calcium carbonate from soil.

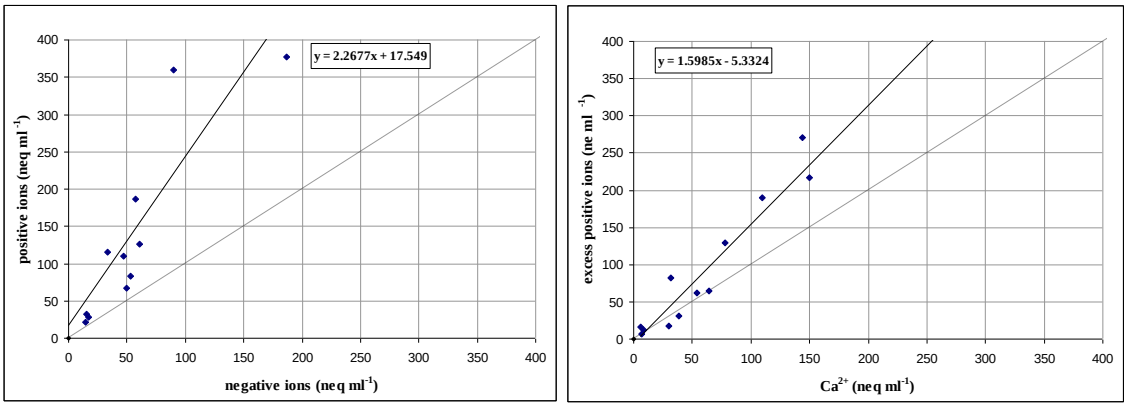

Figure 7.3 Ion balance and correlation between the excess of positive ions and calcium.

Large amounts of Mg^{2+} in the coarse fraction could also be due to entrainment of soil dust. The equivalents ratio between the excess of positive ions and calcium is about 1 and 1.9 for $PM_{2.5}$ and $PM_{2.5\text{-}10}$, respectively. This indicates that coarse particles are influenced by an additional source of Ca^{2+}, besides soil calcium carbonate. On the other hand, the excess of positive ions could imply that not all the major anionic components were measured. Many researchers have reported that biomass burning contains a significant fraction of water-soluble formate, acetate, oxalate and other organic anions, such as malonate, succinate and glutarate (Song et al., 2005; and references therein).

It was observed that the major inorganic fine particles that were emitted during these flaming fires consist of KCl and NH_4Cl. These compounds are very soluble in water and, consequently, the particles are expected to be active as cloud condensation nuclei

(CCN). Emissions from fires in Mediterranean shrublands may therefore notably contribute to the indirect radiative forcing on a regional scale in this region. Petters et al. (2009) examined the hygroscopic properties of aerosols freshly emitted from laboratory biomass burning experiments, concluding that most particles are CCN active at the point of emission and do not require conversion in the atmosphere to more hygroscopic compositions before they can participate in cloud formation and undergo wet deposition. The constituents of the K- and Cl-rich particles are organically bound and/or present in the fluids of the vegetation, volatilised during the combustion process and afterwards converted into the particulate phase by nucleation or condensation. Elemental mass ratios of K and Cl to elemental carbon (Table 7.3) compare to the signatures of cerrado and savannah fire emissions. Echalar et al. (1995) presented K/EC ratios in the range 0.007-1.14, showing lowest values for wood smoke and forest fires, and maximum values for cerrado and savannah biomass burning.

Table 7.3 Potassium and chlorine to elemental carbon mass ratios obtained in different studies.

	This study	Yamasoe et al. (2000)		Ferek et al. (1998)	Maenhaut et al. (1996)		Andreae et al. (1998)
	Mediterranean shrubland	Tropical forest and cerrado in Amazonia		Forest, cerrado and pasture fires in Brazil	Prescribed fires in South Africa		Savannah fires
	Flaming	Flaming	Smouldering		Flaming	Smouldering	
Cl/EC	0.24	0.17	0.15	0.44	0.31	0.22	2.39
K/EC	0.48	0.24	0.20	0.60	0.20	0.17	0.62

Table 7.4 presents the mass percentage of trace elements in smoke particulate matter. Some trace element measurements have been also presented for sugar cane (Lara et al., 2005), rice straw (Viana et al., 2008), wheat straw (Sahai et al., 2007), agricultural burning (Jimenez et al., 2006), wind tunnel derived profiles for herbaceous and wood fuels (Turn et al., 1997) and prescribed burnings in pine-dominated forests in Georgia, USA (Lee et al., 2005). More than 30 metal elements have been detected in the smoke samples from Lousã Mountain, representing about 2.5 % of the PM_{10} mass. The coarse fraction was the richest in these trace components. The dominant elements were iron, barium, thulium and zinc. Gaudichet et al. (1995) also found high concentrations of Fe in savannah biomass burning aerosols, attributing its origin to soil remobilisation processes during the fires and to terrigeneous particles deposed on vegetation. As it occurred in aerosols from Lousã Mountain, Fe was predominantly found in the coarse particles, suggesting a crustal origin.

Table 7.4Trace elements (expressed as wt % of particle mass) obtained in samples from Lousã Mountain and values from the literature.

Element	$PM_{2.5}$ Lousã	$PM_{2.5-10}$ Lousã	PM_2, $PM_{2.5}$ or PM_4 (literature)	Biome type (literature)
Sc	0.0003±0.0002	0.0038±0.0007		
Cr	0.015±0.025	0.017±0.037	0.013-0.023	Cerrado
			bld-0.014	Tropical broadleaf
Fe	0.30±0.38	1.7±1.2	0.05-1.3	Cerrado
			0.03-0.9	Tropical broadleaf
Co	0.0004±0.0003	0.0047±0.0087		
Zn	0.049±0.057	0.18±0.13		
As	0.0052±0.0011	0.0052±0.0008		
Se	0.0003±0.0003	0.0013±0.0028	0.0012-0.0034	Cerrado
			0.0020-0.0028	Tropical broadleaf
Br	0.010±0.0058	0.025±0.0009	0.042-0.057	Cerrado
			0.029-0.051	Tropical broadleaf
Rb	bdl	0.0060±0.0009	0.013-0.015	Cerrado
			0.008-0.012	Tropical broadleaf
Sr	bdl	bdl	0.004-0.006	Cerrado
			bdl-0.003	Tropical broadleaf
Zr	0.0023±0.0040	0.033±0.0037	bdl-0.018	Cerrado
			bld	Tropical broadleaf
Mo	0.025±0.041	0.0023±0.0025		
Cd	0.0010±0.0002	bdl		
Sb	0.0008±0.0002	0.0006±0.0013		
Cs	0.0001±0.0001	0.0013±0.0003		
Ba	0.027±0.021	0.24±0.19		
La	0.0005±0.0004	0.011±0.0012		
Ce	0.0035±0.0047	0.021±0.0026		
Pr	0.0003±0.0004	0.0019		
Nd	bdl	0.0019±0.0018		
Sm	0.0003±0.0003	0.0017±0.0004		
Eu	0.0001±0.0000	0.0001±0.0002		
Tb	bdl	0.0001±0.0002		

Tm	0.24±0.55	bdl
Yb	0.0002±0.0002	0.0004±0.0009
Hf	0.0011±0.0000	0.0011±0.0025
W	bdl	0.0001±0.0002
Th	0.0002±0.0004	0.0018±0.0004
U	0.0003±0.0002	0.0002±0.0003
Sum	0.69±0.06%	2.24±0.28%

bdl - below detection limit.

Data sources for savannah are Andreae et al. (1998), Cachier et al. (1995) and Maenhaut et al. (1996).

Data source for grassland is Ferek et al. (1998).

Data sources for cerrado and tropical broadleaf are Ferek et al. (1998), Ward et al. (1992), and Yamasoe et al. (2000).

However, it should be taken into account that iron is also a component of vegetation and takes part in physiological processes (Gonçalves et al., 2002; Zocchi and Cocucci, 1990). Estimates of zinc emissions by tropical savannah fires by Echalar et al. (1995) indicate that the contribution of this source should be taken into account to understand the biogeochemical cycles of this element. Zinc is present in the cytoplasms of plants and may be associated with the combustion of vegetation (Andreae et al., 1998). Many rare earth elements (REE), such as La, Ce, Nd, Pr, Sm, Tb, Tm and Yb, take place in physiological processes of plants, playing also an important role in soil microorganisms with their biosorption ability and produce organic acids that can serve as phosphate solubilisers. It has been demonstrated that many plants are accumulators of trace metals (Babula et al., 2008; Pratas et al., 2005), including REE and elements yielding medium- and long-lived radionuclides (e.g. Sc, Cr, Rb, Cs, Ba, U, etc.). Many of these elements have been detected in plants such as those growing in Lousã Mountain (Pratas et al., 2005). Thus, biofuel burning may result in the volatilisation of these trace metals which then undergo condensation or gas-to-particle type reactions, adsorbing on the surface of pre-existing aerosols. In addition, plant debris or partially combusted foliage ash may contribute to the detection of trace metals, principally in coarse aerosol particles.

Based on the classification (cambisoils) and the average composition of soil from Lousã Mountain, enrichment factors were calculated (McKenzie et al., 2008) with Th as reference element, since it was found to be a major crustal metal in this region (Ferreira,

2004). Assuming that Th is only associated with soil-derived particles, and that the ratio of the element *X* versus Th is known in the parent soil, the percentages of *X* from noncrustal origin were derived:

$$X_{noncrustal}\ (\%)=(E_X\text{-}1)/E_X \times 100 \qquad (4)$$

where E_X represents the enrichment factor of element *X* in the particulate matter relative to the crust. In this case, the equation used for the E_X calculation was

$$E_X=(X/Th)_{PM}/(Th/X)_{soil} \qquad (5)$$

These calculations showed that, in $PM_{2.5\text{-}10}$, up to 80% for As and 50% for La were of crustal origin. The soil-derived dust represented about 4, 28, 21 and 6% of Ba, Co, Cr and Zn concentrations in coarse particles, respectively. It was also estimated that Fe had a significant part of its concentration (up to 28%) imposed by the soil contribution. These values must be considered as an upper limit according to the hypothesis attributing all the measured Th to the crustal source.

Due to the scarcity of data, a comparison with values from other authors is only possible for a few metals (Table 7.4). For these, concentrations in the smoke plumes of the experimental fires in Lousã Mountain are not very far from those obtained in Amazonia and African savannah. It should be noted, however, that in addition to the biome specificities and high variability of combustion efficiencies, different sampling strategies (ground-based measurements, masts, aircrafts, PM_2, $PM_{2.5}$, PM_4, etc.) may render a comparison of data very tricky.

7.4 Conclusions

This study includes novel data on emissions of trace gases from fires in a Mediterranean shrubland. The low degree of fuel packing in this type of ecosystem contributed to very high-intensity flaming combustion and to the sampling of very fresh plumes, even in seasonal and humidity conditions not yet prone to natural fire development. Under these conditions, emissions of CO_2 and NMHC were higher than those reported for fires in other biome types. Contrarily, emissions of the species that are

favoured by the smouldering phase, such as CO, presented EFs lower than values proposed for fires in the African savannah and Amazonia. The emission factor for CO_2 equivalent to the emitted CH_4 from the shrubland burnings was 29.4 g kg^{-1}, which is 2.0% of the original 1700 g kg^{-1} for CO_2 only. The average emission factors for other species were as follows (g kg^{-1} of dry fuel consumed): 1.8 (methanol), 1.7 (propene), 1.3 (ethane), 3.4 (acetylene), 1.3 (NH_3) 0.122 (N_2O), < 0.3 (NO_x), 0.16 (SO_2) and 3.4 ($PM_{2.5}$). $PM_{2.5}$ represented around 80% of the PM_{10} mass. More than 30 trace metals and water-soluble ions have been determined in smoke aerosols, representing in total an average contribution of about 7% to the PM_{10} mass. Approximately 50% of the particulate mass is carbonaceous in nature with a clear dominance of organic carbon and much lower EC values than those reported in the literature.

The comprehensive chemical characterisation data set obtained during this experiment is potentially very useful for numerical models to evaluate the impact of forest fires on the microscale to regional-scale atmosphere in the Mediterranean region. Taking into account that, besides emission inventories, climate change, atmospheric photochemical and source apportionment models use emission profiles which should reflect the regional characteristics of biofuels, and that considerable uncertainties remain regarding the magnitude of carbon exchanges between the wildland burning and the atmosphere, it has yet to be estimated more specific emission profiles for wildfires in wood-dominated forests in Southern Europe, especially under extreme weather conditions.

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CHAPTER 8

Chapter 8. Inventory of fine particulate organic compound emissions from residential wood combustion in Portugal

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Abstract

In the early fall of 2010 a survey questionnaire was conducted to assess residential wood combustion (RWC) practices in the 18 districts of mainland Portugal. This paper describes and analyses the results from a bottom-up approach, based on this telephone survey, which enabled the characterisation of RWC practices in each district. Additionally, emission factors and source profiles obtained from different RWC tests, allowed the estimation of CO, CO_2, $PM_{2.5}$ and particulate organic compound emissions on a country-scale. The type and number of RWC appliances, each with their specific emission factors and the amount and type of fuel used vary significantly on a district scale. The energy consumption in RWC appliances was estimated to be 35342 TJ y^{-1}. The estimated emissions of $PM_{2.5}$ from RWC in Portugal (10.96 kt y^{-1}) represent 30% of the estimate for different source activities reported in a recent inventory. The national emissions of OC and EC were estimated to be 5.32 and 0.53 kt y^{-1}, respectively. It was also estimated that the total CO_2 emissions from RWC in Portugal are 1.7 Mt y^{-1}. The levoglucosan emissions contribute with between 7.8% and 16.1% of $PM_{2.5}$ emissions from RWC.

Keywords: Survey questionnaire, wood species, burning appliances, emission factors, inventory.

8.1 Introduction

Nowadays, most developed countries suffer from a nearly total dependence on fossil fuels for energy production, in economic and social activities. With the emergence of environmental politics and the imminent depletion of fossil fuels, there is a strong encouragement to change to renewable energy sources. The use of biomass for energy production is being promoted to decrease the dependence on fossil fuels. However, biomass burning is one of the major sources of atmospheric particulate matter (PM), which has significant impacts on human health (Lighty et al., 2000), regional and global air quality (Lelieveld et al., 2001) and climate (Chen et al., 2010; Langmann et al., 2009).

In Europe, emissions from residential wood combustion (RWC) are one of the major sources of atmospheric aerosol mass, mainly in winter (Gelencsér et al., 2007; Krecl et al., 2008; Lanz et al., 2007; Puxbaum et al., 2007). Modelling results indicated that in Portugal 18% of PM_{10} (particulate matter less than 10 micrometers in aerodynamic diameter) could be related to this emission source (Borrego et al., 2010). Source apportionment results from a $PM_{2.5}$ (PM less than 2.5 micrometers in aerodynamic diameter) database obtained in a coastal/rural area in Portugal, showed that 52–69% of the organic carbon in this area can be attributed to residential wood combustion (Gelencsér et al., 2007).

In this paper, data from a number of source burning tests conducted with several Portuguese wood species (Alves et al., 2011; Fernandes et al., 2011; Gonçalves et al., 2011) were used to assemble a national inventory of emissions. These emissions include $PM_{2.5}$, organic and elemental carbon (OC and EC), carbon monoxide and carbon dioxide (CO and CO_2) and various individual organic compounds that are released from RWC (fireplaces and woodstoves) in Portugal. Estimations of the contributions of RWC to $PM_{2.5}$ emissions and the associated organic compounds are hard to obtain, because the emission factors of characteristic wood smoke markers, such as anhydrosugars, resin acids, phenolic compounds, certain phytosterols and polycyclic aromatic hydrocarbons (PAHs) vary greatly with wood type and burning equipment (Gonçalves et al., 2011). Besides, the amounts and types of wood burned, the categories of burning appliances can also differ significantly from region to region. In spite of its complexity, it is possible to estimate the wood smoke emissions throughout the country by weighting the emission profiles from RWC tests, in proportion to the availability of biofuels and the amounts burned in each

region. In addition to the emission factors, a comprehensive knowledge of RWC activity data and its spatial distribution, which are not available in national statistical databases, is required. As a consequence, only a few studies (Fine et al., 2002a; Pastorello et al., 2011) have used a bottom-up approach to calculate particulate matter emissions from RWC and their spatial distribution. At the present moment, a country-scale accounting of specific particulate organic compound emissions has only been done in the USA (Fine et al., 2002a). The work presented here for Portugal is a demonstration of the feasibility of this bottom-up methodology to infer the emissions of domestic biomass burning at the European scale.

A survey to assess the RWC practices was conducted in mainland Portugal in the early fall of 2010. This survey questionnaire aimed to obtain data on wood-burning activity, appliance ownership, and wood species availability in the households of 18 districts of the country. The results were used in conjunction with wood smoke source profiles to quantify the extent of regional variations in particulate organic compound emissions.

8.2 Material and Methods

8.2.1 Survey questionnaire

The survey questionnaire was conducted by telephone calls between 21 September and 11 October 2010 by a market research company, working under contract for the University of Aveiro. Telephone surveys have the advantage of using an interactive interviewer who can explain stove types, wood use units and make sure the survey is complete. The computer-assisted telephone interviewing (CATI) system has been used. Families residing in the 18 districts of mainland Portugal were randomly chosen in the telephone book. To perform the survey research quota sampling, based on last Portuguese census data (2001), was drawn up. The mainland Portuguese territory was divided into districts forming 18 strata. The determination of the "correct" sample size per strata was based on the application of statistical equations (Hill and Magalhães, 2002; Pestana and Gageiro, 2005), which required the following information: number of inhabitants per district, desired error level (5%) and desired level of confidence (95%). Young people (< 18 years old) were ruled out, both because of the difficulties involved in interviewing them

and because many research questions did not apply to them. From the 2387 effective respondents, a total of 806 positive answers were obtained, i.e., house owners who have declared the use of RWC, while the remaining 1581 households do not use wood. The survey questionnaire included questions to estimate the amounts of wood consumption for different categories of fuels and the number of RWC appliances in use. The statistical errors (95% confidence interval) of the questionnaire have been calculated through the usual formulas based on the number of interviews in the sample and the real variability of the estimated wood combustion (Hill and Magalhães, 2002; Pestana and Gageiro, 2005). The content of the survey questionnaire can be found in the Supplementary Material section (Table A4).

8.2.2 Emission factors

In this study, the geographical distribution of appliance types and total wood use (data from survey questionnaire) were combined with source testing results and wood species availability to estimate an overall emission profile for RWC, per district, in Portugal.

To ensure the inclusion of the most prevalent wood species within the RWC program, the top seven predominant tree species in Portugal were chosen: *Pinus pinaster* (Maritime pine), *Eucalyptus globulus* (Eucalypt), *Quercus suber* (Cork oak), *Acacia longifolia* (Golden wattle), *Quercus faginea* (Portuguese oak), *Olea europea* (olive) and *Quercus ilex rotundifolia* (Holm oak). The selection was done in accordance with the Portuguese Forest Inventory (2005). In addition, the emissions from biomass briquettes and pellets made of wastes from forest cleaning activities and wood processing industries, used commonly in Portugal for home heating, were also studied. A detailed speciation of organic compounds in wood smoke from these biofuels (mg g^{-1} OC) was provided in a preceding work (Gonçalves et al., 2011). In Fernandes et al (2011) study, emission factors per kilogram of wood burned for $PM_{2.5}$, OC, EC, CO and CO_2 during the combustion in fireplace and woodstove of the dominant wood species in mainland Portugal were obtained (Table 8.1). These emission factors are average values of 3 or 4 combustion experiments, which tried to simulate the residential use of burning appliances in the wintertime. During each combustion experiment, which lasted between 45 and 90 min., about 6 kg of wood was burned, using three consecutive batches of around 2 kg each. The first combustion

experiment of each series included the start-up phase after a batch of wood logs had been added to the combustion chamber at ambient temperature. The other combustion experiments of each series were initiated with the load of a batch of fuel to the combustion chamber containing burning char, and included the intermediate and burn-out phases. Thus, the average emission factors represent the daily pattern of wood use among Portuguese families.

Table 8.1 $PM_{2.5}$, carbonaceous constituents, CO and CO_2 emission factors (g kg^{-1} biomass burned, dry basis).

Appliances	Wood species	$PM_{2.5}$	OC	EC	CO	CO_2
Woodstove	Maritime pine	5.2±4.3	2.5±2.5	0.61±0.43	57.1±19.0	1670±251
	Golden wattle	7.9±4.3	4.1±2.65	0.29±0.18	96.5±24.0	1584±413
	Holm oak	5.8±3.9	3.0±2.1	0.23±0.10	63.7±18.6	1632±315
	Eucalypt	10±6.7	5.2±4.0	0.37±0.30	67.6±14.3	1548±259
	Olive	8.7±4.5	4.6±2.2	0.46±0.24	64.9±15.7	1725±320
	Cork oak	8.3±6.1	4.8±3.4	0.42±0.33	99.2±30.8	1604±414
	Portuguese oak	13±8.3	6.2±4.6	0.32±0.15	85.9±12.8	1573±200
	Briquettes/Pellets	7.1±4.8	3.7±3.0	0.18±0.12	62.9±15.8	1636±261
Fireplace	Maritime pine	6.9±3.6	2.9±1.3	0.62±0.49	51.1±6.89	1735±132
	Golden wattle	7.8±6.2	3.5±3.1	0.34±0.26	61.8±3.79	1697±68.7
	Holm oak	13±8.3	7.2±4.0	0.30±0.11	61.8±8.17	1675±147
	Eucalypt	12±7.6	5.1±3.9	0.36±0.36	78.9±7.35	1585±72.7
	Olive	21±10	9.1±5.7	0.39±0.16	81.0±8.02	1743±193
	Cork oak	18±10	10±5.2	0.68±0.40	85.5±21.9	1662±307
	Portuguese oak	14±9.7	6.1±3.4	0.32±0.20	78.5±17.6	1641±40.7
	Briquettes/Pellets	12±7.7	5.9±4.2	0.29±0.25	58.3±16.9	1691±54.5

The chromatographically resolved organic compounds extracted from the smoke samples included the *n*-alkane homologous series from C_{14} to C_{34}, *n*-alkenes from C_{16} to C_{28}, PAHs, *n*-alkanals, ketones, *n*-alkanols, terpenoids, phenolic compounds, phytosterols, alcohols, resin acids, *n*-alkanoic acids, *n*-diacids, unsaturated acids and alkyl esters of acids (Gonçalves et al., 2011). The main PAH species present in wood smoke were retene, pyrene, fluoranthene, phenanthrene and benzo(a)pyrene. From the 180 individual organic compounds inventoried in the smoke samples, 7 phenolic compounds (vanillic acid, syringic acid, coniferyl alcohol, catechol, methylcatechol, pyrogallol and vanillin) (Table 8.2), 4 resin acids (dehydroabietic acid, isopimaric acid, pimaric acid and abietic acid) (Table 8.3), 3 anhydrosugars (galactosan, mannosan and levoglucosan) (Table 8.4), 2 phytosterols (stigmasterol and *β*-sitosterol) (Table 8.5) and 11 PAHs (retene,

benzo(a)pyrene equivalents (BaPE), benzo(a)anthracene (BaA), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IcdP), dibenzo(a,h)anthracene (DBA), benzofluranthenes (BFs), Phenanthrene (Ph), Fluoranthene (Flu), Pyrene (Pyr) and Chrysene (C)) (Table 8.6) have been chosen to demonstrate regional variations in residential wood combustion source profiles. The BaPE is an index that parameterises the health risk for humans related to the exposition to ambient carcinogenic PAH (Alves, 2008). For its calculation the following equation was used:

$$BaPE = 0.06 \times BaA + 0.07 \times BFs + BaP + 0.6 \times DBA + 0.08 \times IcdP$$

where

BaA – Benzo(a)anthracene

BFs – Benzofluranthenes

BaP – Benzo(a)pyrene

DBA – Dibenzo(a,h)anthracene

IcdP – Indeno(1,2,3-cd)pyrene

These phenolics, anhydrosugars, acids, sterols and retene have been reported as good tracers for biomass burning since their high emission rates increase the likelihood that the compounds can be detected in ambient samples. They are single tracers of this particular source, which facilitates the chemical mass balance calculations. Additionally, they remain mostly unchanged during the transport period between source and receptor sites, due to their slow atmospheric reactive capacity (Fine et al., 2002a). These characteristics were taken into account when the different compounds were chosen.

Table 8.2 Phenolic compounds emission factors (g kg^{-1} biomass burned, dry basis).

Appliances	Wood Species	Vanillic acid	Syringic acid	Coniferyl alcohol	Catechol	Methyl catechol	Pyrogallol	Vanillin
Woodstove	Maritime pine	0.016	0.0003	0.0004	0.021	0.020	0.005	0.010
	Golden wattle	0.010	0.009	0.003	0.093	0.093	0.068	0.147
	Holm oak	0.017	0.039	0.002	0.069	0.059	0.096	0.026
	Eucalypt	0.007	0.045	0.001	0.053	0.056	0.215	0.025
	Olive	0.004	0.008	0.016	0.007	0.004	---	0.041
	Cork oak	0.032	0.067	0.008	0.175	0.140	0.256	0.046
	Portuguese oak	0.026	0.091	0.002	0.334	0.263	0.675	0.052
	Briquettes/Pellets	0.052	0.103	0.004	0.111	0.142	0.208	0.035
Fireplace	Maritime pine	0.005	0.0001	0.002	0.021	0.034	0.004	0.004
	Golden wattle	0.008	0.017	0.016	0.072	0.110	0.104	0.029
	Holm oak	0.029	0.122	0.036	0.127	0.089	0.213	0.075
	Eucalypt	0.007	0.053	0.001	0.134	0.099	0.267	0.017
	Olive	0.008	0.012	0.025	0.062	0.051	0.154	0.034
	Cork oak	0.008	0.026	0.029	0.116	0.096	0.255	0.163
	Portuguese oak	0.018	0.055	0.016	0.131	0.106	0.224	0.088
	Briquettes/Pellets	0.039	0.048	0.002	0.143	0.092	0.165	0.055

(---) not detected

Table 8.3 Resin acids emission factors (g kg^{-1} biomass burned, dry basis).

Appliances	Wood species	Dehydroabietic acid	Isopimaric acid	Pimaric acid	Abietic acid
Woodstove	Maritime pine	0.192	0.034	0.242	0.013
	Golden wattle	0.047	0.008	0.061	0.017
	Holm oak	0.035	0.005	0.043	0.001
	Eucalypt	0.011	0.002	0.013	0.002
	Olive	0.024	0.004	0.028	0.014
	Cork oak	0.063	0.022	0.102	0.045
	Portuguese oak	0.122	0.011	0.148	0.008
	Briquettes/Pellets	0.061	0.017	0.083	0.001
Fireplace	Maritime pine	0.440	0.056	0.512	0.045
	Golden wattle	0.006	0.004	0.012	0.002
	Holm oak	0.002	0.001	0.003	---
	Eucalypt	0.045	0.004	0.050	---
	Olive	0.042	0.005	0.047	0.0003
	Cork oak	0.007	0.0003	0.008	0.002
	Portuguese oak	0.083	0.007	0.089	0.003
	Briquettes/Pellets	0.037	0.014	0.054	0.000

(---) not detected

Table 8.4 Anhydrosugars emission factors (g kg^{-1} biomass burned, dry basis).

Appliances	Wood species	Galactosan	Mannosan	Levoglucosan
Woodstove	Maritime pine	0.126	0.331	0.424
	Golden wattle	0.190	0.310	0.918
	Holm oak	0.143	0.236	0.525
	Eucalypt	0.278	1.185	0.948
	Olive	0.028	0.043	0.142
	Cork oak	0.333	0.546	1.639
	Portuguese oak	0.789	1.527	3.444
	Briquettes/Pellets	0.611	0.802	1.512
Fireplace	Maritime pine	0.244	0.101	0.604
	Golden wattle	0.199	0.165	0.759
	Holm oak	0.358	0.144	0.996
	Eucalypt	0.457	0.179	1.821
	Olive	0.166	0.308	0.711
	Cork oak	0.249	0.147	1.058
	Portuguese oak	0.359	0.138	1.507
	Briquettes/Pellets	0.628	0.607	0.735

Table 8.5 Phytosterols emission factors (g kg^{-1} biomass burned, dry basis).

Appliances	Wood species	Stigmasterol	*β*-Sitosterol
Woodstove	Maritime pine	---	0.007
	Golden wattle	0.003	0.008
	Holm oak	0.001	0.015
	Eucalypt	0.0002	0.021
	Olive	0.002	0.028
	Cork oak	0.0003	0.026
	Portuguese oak	0.001	0.015
	Briquettes/Pellets	0.002	0.012
Fireplace	Maritime pine	0.00002	0.043
	Golden wattle	0.007	0.010
	Holm oak	0.002	0.039
	Eucalypt	0.0003	0.020
	Olive	0.001	0.020
	Cork oak	0.0003	0.041
	Portuguese oak	0.001	0.030
	Briquettes/Pellets	0.001	0.011

(---) not detected

Table 8.6 PAH emission factors (μg kg^{-1} biomass burned, dry basis).

Appliances	Wood species	Retene	BaPE	BaA	BaP	IcdP	DBA	BFs	Ph	Flu	Pyr	C
Woodstove	Maritime pine	9644	78	186	96	52	8	253	247	356	1208	254
	Golden wattle	1167	165	315	166	88	12	285	736	892	1297	321
	Holm oak	1122	428	337	440	241	30	880	1201	1496	1932	351
	Eucalypt	636	337	522	374	213	25	674	1181	1312	1656	388
	Olive	949	534	808	482	280	33	971	1348	1857	2503	645
	Cork oak	483	131	171	79	32	44	299	459	389	824	266
	Portuguese oak	435	117	103	78	37	27	248	258	299	670	180
	Briquettes/Pellets	1910	112	143	72	40	6	219	343	358	416	178
Fireplace	Maritime pine	9356	281	312	218	111	17	362	493	662	906	306
	Golden wattle	511	376	451	293	158	18	473	837	1235	1756	409
	Holm oak	200	1014	1303	785	387	45	1311	2824	3520	5095	1046
	Eucalypt	136	---	94	63	33	---	102	155	296	375	95
	Olive	1221	630	735	493	273	33	733	861	1430	2549	564
	Cork oak	38	323	398	252	128	18	378	1431	1105	1600	376
	Portuguese oak	48	567	936	646	323	69	882	1325	1977	3350	660
	Briquettes/Pellets	486	---	63	25	16	---	52	223	248	287	74

BaPE – Benzo[a]pyrene equivalency
BaA – Benzo[a]anthracene
BaP – Benzo[a]pyrene
IcdP – Indeno[1,2,3-cd]pyrene
DBA – Dibenzo[a,h]anthracene
BFs – Benzofluoranthenes
Ph – Phenanthrene
Flu – Fluoranthene
Pyr – Pyrene
C – Chrysene
(---) not detected

8.2.3 Calculation of emissions

Since there are different categories of emission sources, the Intergovernmental Panel on Climate Change (IPCC) had a need to create different ways of calculating the emissions, described as Tiers (Tier 1, Tier 2 and Tier 3). Tier 1 corresponds to a generic emission factor for particles or a particular greenhouse gas and a particular fuel. The Tier 2 approach is similar to the Tier 1 approach, using activity data and emission factors to estimate the emissions. The main difference is that the detailed methodology requires more fuel, technology and country-specific information. The Tier 3 methodology allows a modelling-based approach using more detailed appliance population data and applies more technology-specific emission factors. In other words, each Tier has an associated increasing level of detail and accuracy (IPCC Guidelines, 2006).

In this particular case, to estimate the annual emissions, the Tier 2 approach was followed, using district-specific information on activity data and emission factors (EMEP/EEA, 2009):

$$E_i = \Sigma_{j,k}\, EF_{i,j,k} \times A_{j,k}$$

where

E_i = annual emission of pollutant i,

$EF_{i,j,k}$ = emission factor of pollutant i for appliance type j and fuel k

$A_{j,k}$ = annual consumption of fuel k in appliance type j

Special attention has been taken to identify outliers in order to assure corrective actions. Wood consumptions <100 kg y^{-1} or >10 t y^{-1}, and total number of hours of usage <50 h y^{-1} or >2000 h y^{-1} were defined as anomalous observations. However, no extreme values were observed; thus, corrections or replacements from the original data were not made. The method for calculating composite regional source profiles took several steps. First, the amount of wood burned in each of the 18 districts of mainland Portugal was taken from the survey questionnaire (Table A4, supplementary material A4). Values given in Euros or cubic meters (m^3) were converted to mass (ton) of wood burned using, respectively, the average price per ton of each type of wood per district and wood densities (kg m^{-3}), considering a percentage of compaction to account for void volumes (Franscescato et al.,

2008; Xue and Wakelin, 2006). Second, total wood consumption in each district was divided into wood burned in closed appliances and wood burned in open appliances. In fact, the answers to the questionnaire regarding the combustion appliances were broken down into two general categories: (a) open appliances (fireplace, wood burning furnace and other open appliances), and (b) closed appliances (woodstove, salamander stove, oven and other closed appliances). Third, for the remaining wood species for which source tests were not performed, emission factors were estimated on the basis of the averaged results for the other woods. For the application of emission factors for each wood type and appliance (which are given in dry basis) to activity data, the wet weight of the wood was converted to dry weight. An average of 13% was assumed for the moisture content of the wood (Gonçalves et al., 2011). Once the total emissions have been calculated for the households surveyed in a given district ($Emissions_{surveyed}$), it becomes possible to calculate the estimated emissions for the district in general:

$$Emission_{district} = Emissions_{surveyed} \times (Number_{district} / Number_{surveyed})$$

where $Number_{district}$ is the number of households in the district (number of inhabitants divided by the average number of people per household in that district), and $Number_{surveyed}$ is the total number of households that were surveyed.

For calculating the uncertainties of the emissions of each pollutant in each district, the Tier 1 method was followed. It combines uncertainties using error propagation equations (Monni and Syri, 2003). While calculating the emission for each activity and fuel combination, the relative uncertainty was determined as the square root of the sum of the relative uncertainties in both the fuel use and the emission factors. The absolute uncertainty in the emission of each activity and fuel combination was derived by multiplying the relative uncertainty with the emission value.

8.3 Results and Discussion

8.3.1 Wood consumption

The survey questionnaire allowed us to estimate a total of about 2 Mton y^{-1} of domestic wood consumption in Portugal (Table 8.7). RWC is used by more than 3 million and a half inhabitants, which corresponds to 37% out of the total Portuguese population. The wood use shows a pattern that varies between different regions of the country.

Table 8.7 Wood consumption in mainland Portugal districts.

District	**Users** (%)	**Wood consumption** (t y^{-1} household $^{-1}$)	**95% c.i. average consumption** (t y^{-1} household^{-1})	**Wood consumption** (t y^{-1} district^{-1})	**95% c.i. average consumption** (t y^{-1} district^{-1})
Aveiro	54	1.7	1.2 – 2.1	216 129	160 148 – 272 110
Beja	34	1.3	0.8 – 1.7	26 638	17 635 – 35 642
Braga	46	1.6	1.4 – 1.8	184 534	161 273 – 207 795
Bragança	52	2.8	1.9 – 3.6	78 257	53 412 – 103 101
Castelo Branco	44	2.5	1.8 – 3.1	87 425	65 128 – 109 721
Coimbra	36	2.4	1.7 – 3.1	140 232	98 656 – 181 807
Évora	47	1.4	1.1 – 1.7	43 624	34 424 – 52 823
Faro	25	1.0	0.6 – 1.3	34 652	20 970 – 48 334
Guarda	35	2.2	1.7 – 2.7	53 235	40 273 – 66 198
Leiria	51	1.6	1.2 – 1.9	134 788	103 624 – 165 952
Lisboa	24	0.9	0.8 – 1.0	170 427	150 390 – 190 464
Portalegre	30	1.2	0.8 – 1.5	16 936	12 069 – 21 804
Porto	36	1.3	1.1 – 1.4	243 891	208 456 – 279 325
Santarém	54	1.2	0.9 – 1.5	110 229	81 282 – 139 177
Setúbal	24	1.2	0.9 – 1.4	79 299	64 872 – 93 726
Viana do Castelo	29	1.6	1.1 – 2.1	38 834	25 983 – 51 684
Vila Real	33	2.7	1.6 – 3.8	71 866	43 584 – 100 148
Viseu	62	2.6	1.8 – 3.3	218 852	153 402 – 284 302
Total				**1 949 847**	

RWC use is higher in the inland areas of the country such as Viseu, Bragança and Vila Real, where a more severe cold weather is registered in wintertime, and in districts with dominant rural characteristics like Aveiro, Santarém and Leiria. RWC utilisation decreases in the more urbanised districts, such as Lisboa, or in districts with warmer winter climate, such as Faro in Algarve.

In the households where wood is frequently burned, 43% use fireplaces, while 6% of respondents said that burn wood in barbecues fireplaces. Woodstoves and traditional

ovens represent about 24% of the total number of appliances (Table 8.8). The largest percentage of wood (51%) is burned in fireplaces, while the lowest percentage of wood (0.30 %) is burned in furnaces. The results of the questionnaire indicated an average of 1.3 wood combustion appliances per household. The type of wood combustion appliance influences the emission factors significantly. Therefore, the results of the survey in terms of the different types of wood combustion appliances is of great interest to obtain composite weighted emission factors.

Table 8.8 Appliance distribution (%) and wood consumption by appliance in mainland Portugal.

	Percentage distribution (%)	**Wood Consumption (%)**	**Wood Consumption (t y^{-1})**
Fireplace	43	51	954 652
Woodstove	20	22	411 646
Wood burning furnace	11	12	218 631
Salamander stove	7.8	7.6	143 125
Boiler	7.2	3.3	61 646
Barbecue	5.8	1.5	28 027
Oven	4.3	2.5	46 785
Wood burning water heater	0.57	0.58	10 839
Furnace	0.38	0.30	5 631

It has been estimated that 67–76% of the conventional fireplace and woodstove owners typically use these appliances 2–4 months per year. About 65% of owners stated that they use them 5–7 days $week^{-1}$, while 30–35% burn less frequently (2–3 days $week^{-1}$). It was found that 77% of respondents use between 50 and 100% of the total fuel consumed for heating. On average, 83% of wood consumed is for heating, while the remaining 17% is used for cooking.

Figure 8.1 shows the spatial distribution of wood types burned in open and closed appliances. While Holm oak and cork oak are the most common woods for residential combustion in the southern districts, maritime pine, Portuguese oak and eucalypt present a larger share in northern districts. Around 20% of the house owners burn mixtures of different types of woods.

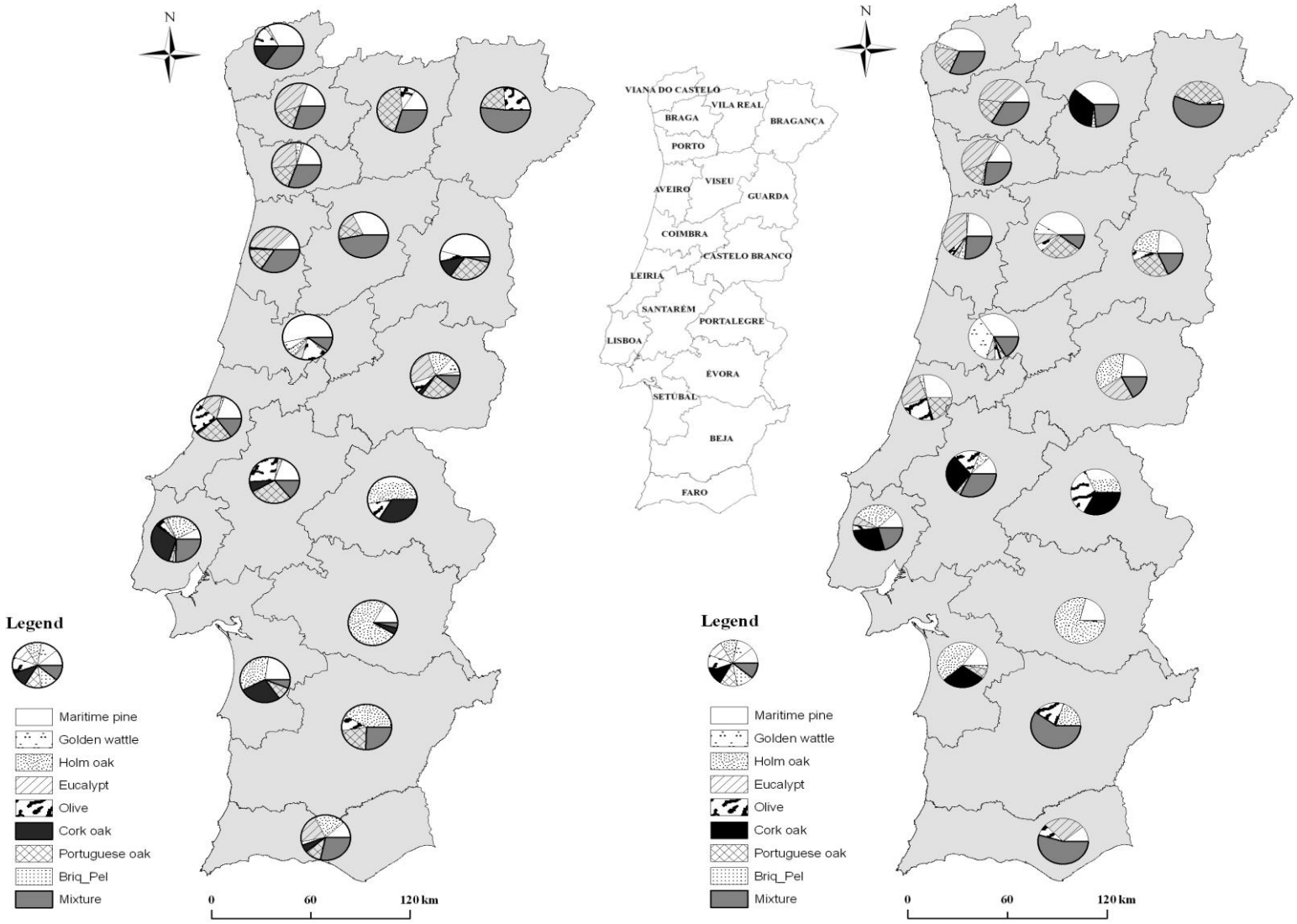

Figure 8.1 Percentages by district of wood species burned by open appliances (left map) and closed appliances (right map).

8.3.2 Estimates of emissions

Emission factors from residential biomass combustion may show wide variation due to the type of fuel, specific combustion appliance, sampling procedures, burning rate and the moisture content of the fuel (Fine et al., 2004; Kowalczk et al., 1981; Lipsky and Robinson, 2006; Wardoyo et al., 2006). To estimate the total emissions in each district, different emission factors for every appliance and every wood type were used. They were weighted by the wood consumption in each type of equipment. For barbecues and innovative closed appliances (e.g. pellet boilers) specific emission factors were not available, and thus they were, respectively, taken as open fireplaces and closed woodstoves. Since it has been determined that the heating value of the representative Portuguese woods range between 17.63 and 20.24 MJ kg^{-1}, and that most of them are included in a very narrow range around 18 MJ kg^{-1} (Telmo and Lousada, 2011), this last value was adopted in calculations.

Depending on the district, total $PM_{2.5}$ emissions ranged from 90 ± 55 t y^{-1} to 1300 ± 830 t y^{-1}. Aveiro and Porto districts presented the highest emissions of $PM_{2.5}$ from RWC. This trend is due to a greater prevalence of fireplaces and barbecues (open appliances), which produce higher fine particle emission rates than woodstoves and other closed appliances. Portalegre is an inland district where the lowest $PM_{2.5}$ emissions were registered. This may be related to the fact that Portalegre is the district with the lowest number of inhabitants of mainland Portugal (Figure 8.2).

The estimated emissions of $PM_{2.5}$ from RWC in Portugal (10.96 kt y^{-1}, which corresponds to 1.11 kg y^{-1} per capita) represent 30% of the estimate of 36.30 kt y^{-1} for different source activities reported in a recent inventory, based on earlier inventories and on national data provided by European Member States (Pulles et al., 2007). This national estimate for $PM_{2.5}$ emissions from several sectors in Portugal amends the previous estimate of 56.20 kt y^{-1} provided by the International Institute for applied Systems Analysis (IIASA). Estimates of $PM_{2.5}$ emissions from RWC in Nordic countries ranged from 1.48 kg y^{-1} per capita in Finland to 8.46 kg y^{-1} per capita in Norway (Karvosenoja et al., 2004). It should be noted, however, that in Scandinavia pellet boilers and other modern higher efficiency appliances dominate, while traditional stoves and fireplaces prevail in Portugal (Alves et al., 2011; Bølling et al., 2009).

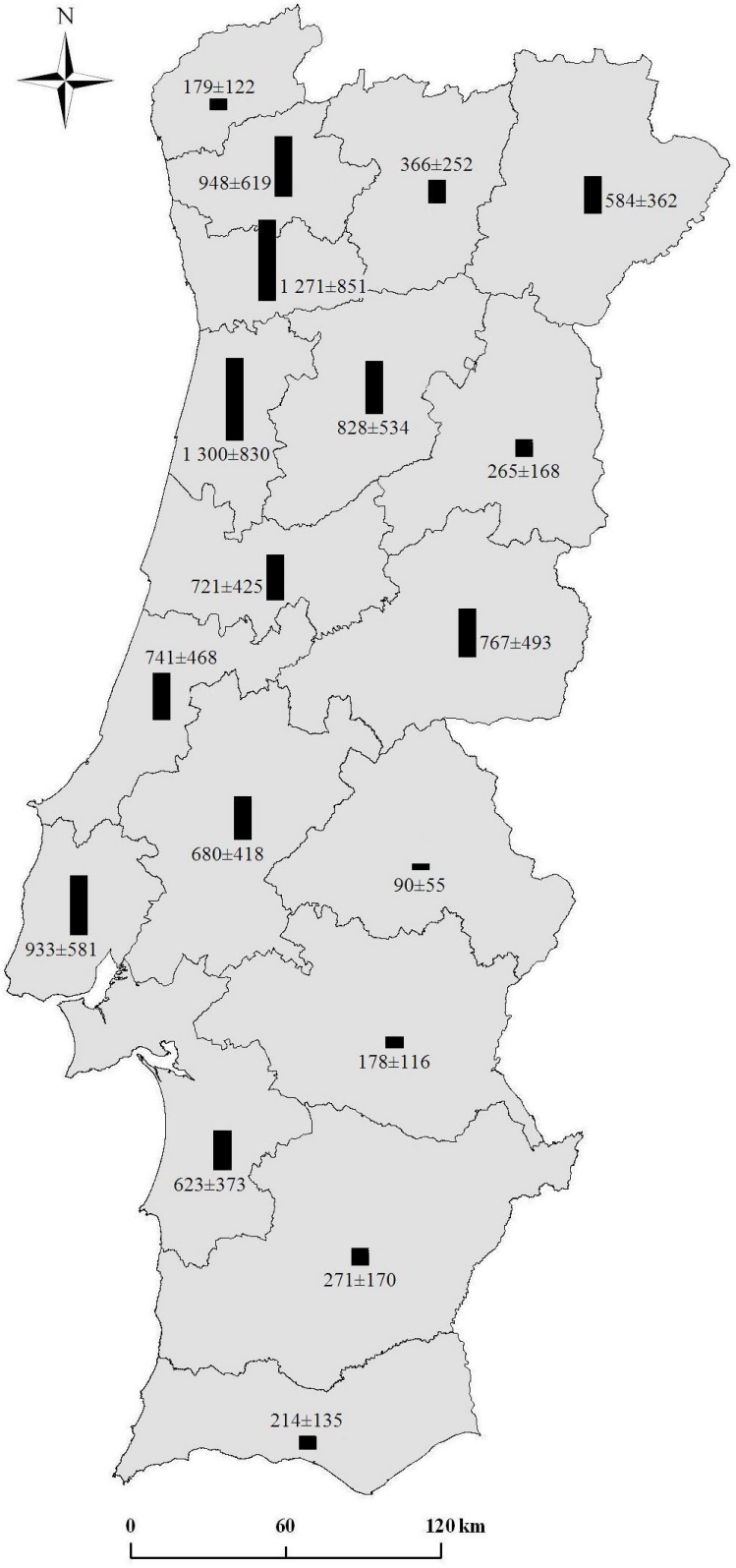

Figure 8.2 Total $PM_{2.5}$ emissions by district (t y^{-1}).

The weighted $PM_{2.5}$ emission factors, based on RWC use patterns, ranged between 210 mg MJ^{-1} in the district of Viseu to 566 mg MJ^{-1} in the district of Beja. The energy consumption in RWC appliances in Portugal was estimated to be 35342 TJ y^{-1}, which corresponds to 3580 MJ y^{-1} per capita. This value is in the range of those reported for Nordic countries: 2170 MJ y^{-1} per capita in Denmark, 7310 MJ y^{-1} per capita in Finland, 4780 MJ y^{-1} per capita in Norway and 4490 MJ y^{-1} per capita in Sweden (Karvosenoja et al., 2004).

The majority of the fine particle mass emitted from RWC consists of organic carbon. This fact has already been documented in previous studies (Fine et al., 2001, 2002b; Schauer et al., 2001). OC emissions per district ranged from 49 ± 28 t y^{-1} (Portalegre) to 635 ± 465 t y^{-1} (Porto). In general, EC has very low emission values ranging between 3 ± 2 t y^{-1} (Portalegre) and 132 ± 4 t y^{-1} (Beja) (Figure 8.3).

The national emissions of OC and EC from RWC were estimated to be 5.32 and 0.53 kt y^{-1}, respectively. OC and black carbon (BC) emissions for the year 2010, in Portugal, considering different types of fuels (coal, biomass, diesel, gasoline, gas and others) were estimated to be 13 kt OC y^{-1} and 8 kt BC y^{-1} (Kupiainen and Klimont, 2004). This suggests that wood burning in domestic appliances contribute, respectively, to about 41% and 7% of the OC and EC national emissions from fuel combustion.

CO and CO_2 emissions ranged from 648 ± 161 t y^{-1} to 9 395 ± 1 994 t y^{-1} and from 14 454 ± 2 611 t y^{-1} to 214 648 ± 30 389 t y^{-1}, respectively. Districts with the highest CO_2 emissions are Porto, Aveiro and Viseu (Figure 8.4). It was estimated that the total CO_2 emissions from RWC in Portugal are 1.7 Mt y^{-1}. An estimate of 52.4 Mt CO_2 from fuel combustion (coal, oil, gas, others) has been reported for Portugal in 2008 (IEA, 2010). Thus, RWC contribute to approximately 3.2% of the CO_2 emissions from fuel combustion.

The CO_2 produced from wood combustion is a renewable energy source because it was previously removed from the atmosphere by the trees producing the wood. This is part of the natural carbon cycle. The life cycle of wood products, from production, use, burning, and replacement is carbon neutral. For this reason, CO_2 is not included in UNFCCC emission inventories.

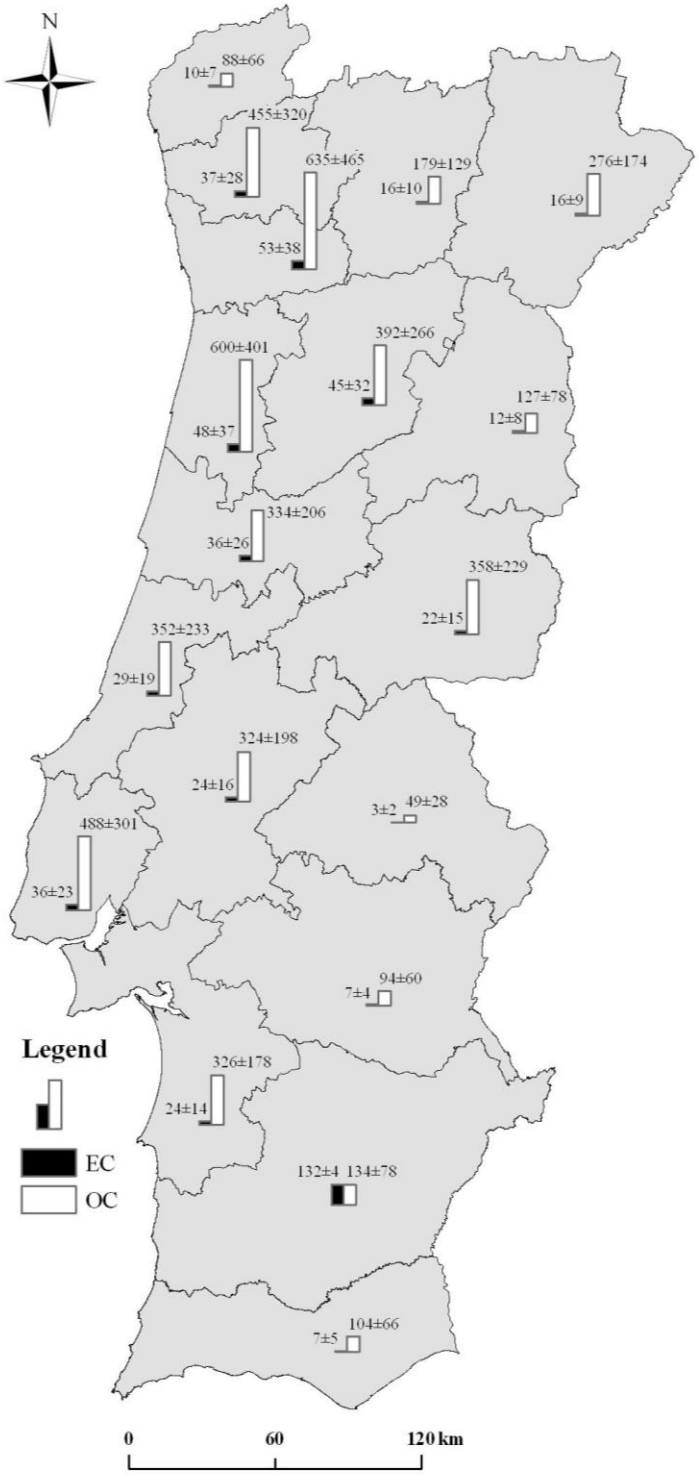

Figure 8.3 EC and OC emissions by district (t y^{-1}).

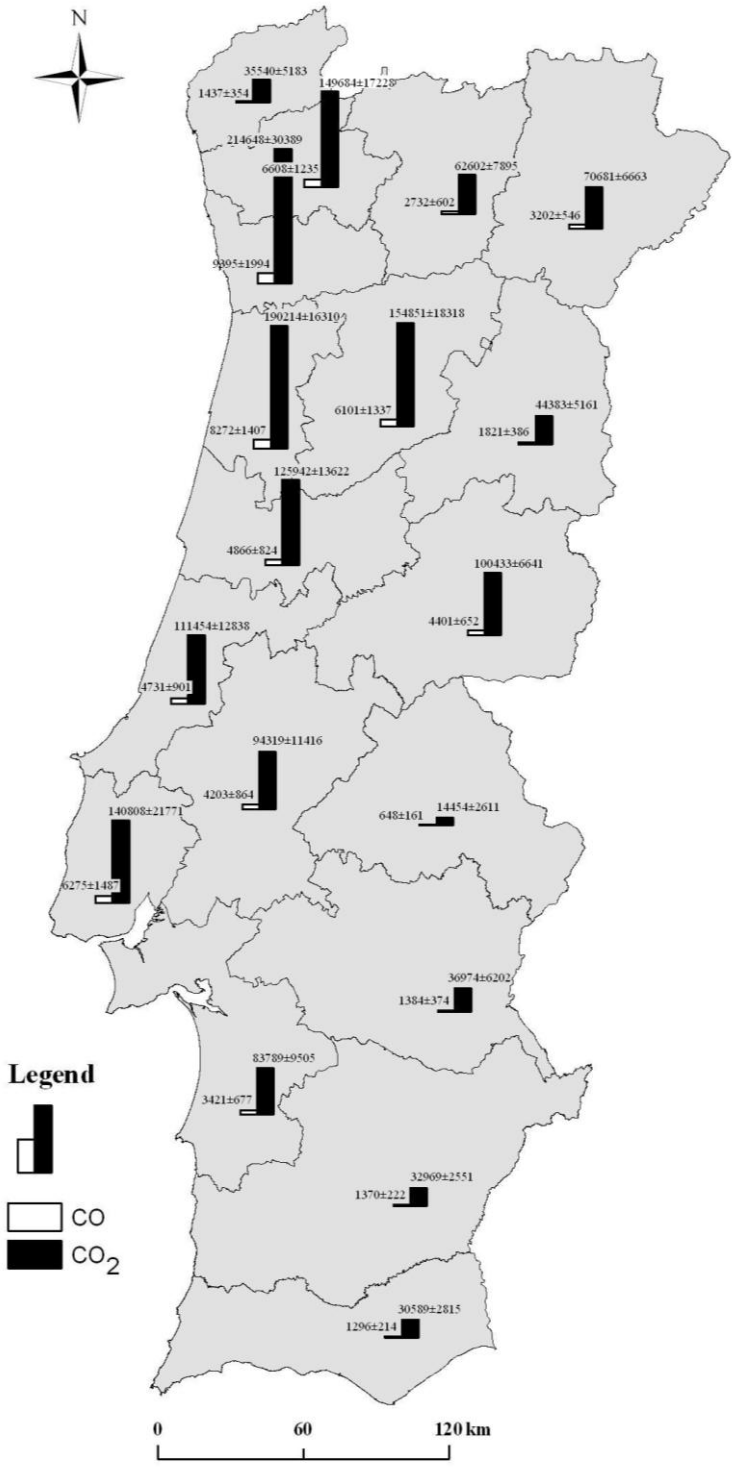

Figure 8.4 Annual emissions of CO and CO_2 by district ($t\ y^{-1}$).

The major organic components of smoke particles from biomass burning are monosaccharide derivatives from the breakdown of cellulose and hemicelluloses, such as levoglucosan, mannosan and galactosan (Gonçalves et al., 2010; Simoneit et al., 1999). Those compounds are non-volatile, existing predominantly in the particle phase as shown in biomass combustion previous works (Gonçalves et al., 2010; Schauer et al., 2001; Schmidl et al., 2008). Figure 1S (Supplementary Material A4) displays the spatial distribution of anhydrosugar emissions. As expected, levoglucosan is the monosaccharide derivative with highest emissions. Levoglucosan emissions ranged from 7.24 t y^{-1} (Portalegre) to 171 t y^{-1} (Porto). Mannosan and galactosan were the second and third most abundant anhydrosugar products from the hemicellulose pyrolysis. Porto, Braga and Aveiro are the districts which present higher emissions rates of mannosan and galactosan. The mannosan values range between 100 t y^{-1} (Porto) and 2.04 t y^{-1} (Portalegre). Galactosan emissions range between 45.7 t y^{-1} (Porto) and 1.83 t y^{-1} (Portalegre).

The very high emission rates of levoglucosan are demonstrated when calculating the fraction of fine particle emissions attributable to this single compound. The levoglucosan emissions contribute with between 7.8% (Beja) and 16.1% (Vila Real) of $PM_{2.5}$ emissions from RWC. Emission rates of levoglucosan between 9 and 16% of the $PM_{2.5}$ mass from domestic burning have been reported for the US (Fine et al., 2002a). The national levoglucosan emissions for Portugal (1.2 kt y^{-1}) are between those estimated for different US EPA regions. Emissions in the US ranged from 0.88 kt y^{-1} in the EPA Region 6 (Arkansas, Louisiana, New Mexico, Oklahoma and Texas) to 2.4 kt y^{-1} in the EPA Region 5 (Illinois, Indiana, Michigan, Minnesota, Ohio and Wisconsin) (Fine et al., 2002a).

Phenolic compounds included polyphenols, methoxyphenols and alkyl phenols. Methoxyphenols have been identified as prominent lignin thermal degradation products (Hawthorne et al., 1988). Figure 2S (Supplementary Material A4) displays the spatial distribution of phenolic compound emissions. The predominant phenolic emissions from RWC are assigned to pyrogallol (Porto – 30 t y^{-1}, Aveiro – 22 t y^{-1} and Braga – 21 t y^{-1}) and catechol (Porto – 14 t y^{-1}). There are some phenolic compounds that are more characteristic of softwood or hardwood smoke. Syringic acid is released in larger amounts by hardwood while vanillic acid is typically released by softwood (Fine et al., 2002a). As it can be seen in Figure 2S (Supplementary Material A4), emissions of syringic acid are

always higher than those of vanillic acid. This is justified by the fact that generally the percentage of hardwood species burned is higher than softwood.

Resin acids, such as pimaric, dehydroabietic, isopimaric and abietic acids, are detected as significant components of softwood emissions, but are found only in trace quantities in the emissions from hardwoods (Gonçalves et al., 2011). Figure 3S (Supplementary Material) shows the regional variation in the relative emissions of these four resin acids. Taking into account that the percentage of hardwood species burned is higher than softwood, these very low emissions are not surprising. The predominant resin acids in emissions from RWC were pimaric acid (0.36–18.8 t y^{-1}) and dehydroabietic acid (0.26–16.0 t y^{-1}). The relative amounts of individual resin acids emitted from RWC vary regionally. Coimbra and Viseu districts are the ones presenting the highest emission yields of those acids. This fact is related to the use of larger amounts of softwood in these districts.

Phytosterols are other kind of biomarker constituents in the smoke from residential wood combustion. The most abundant phytosterol found in smoke samples from residential combustion tests involving Portuguese woods was *β*-sitosterol (Gonçalves et al., 2011). This compound is present in plant lipids (Simoneit, 1998), volatilised during incomplete combustion and subsequently recondensed into the particle phase. Their emission rate can vary widely depending on the wood species being burned (Fine et al., 2001, 2002a). Figure 4S (Supplementary Material A4) shows the spatial distribution of emissions of *β*-sitosterol and stigmasterol. *β*-sitosterol emissions ranged from 0.24 t y^{-1} in Portalegre to 2.82 t y^{-1} in Aveiro. Generally, more *β*-sitosterol is emitted from hardwood combustion than from softwood combustion (Gonçalves et al., 2011). The stigmasterol emissions vary between 0.009 t y^{-1} (Portalegre) and 0.090 t y^{-1} (Castelo Branco). Figure 4S (Supplementary Material A4) depicts the spatial distribution of retene and BaPE emissions. The retene values range between 0.451 t y^{-1} in Viseu, where a higher proportion of softwood is burned, and 0.006 t y^{-1} (Portalegre). PAH emissions, and in particular those of BaPE, are very low in comparison with other compounds studied. Porto, Lisboa and Aveiro districts present the highest emissions, 0.034 t y^{-1}, 0.033 t y^{-1} and 0.030 t y^{-1} respectively. Portalegre district registers the lowest emissions, 0.004 t y^{-1}. The emissions of some individual compounds are presented in Table 8.9. Pyrene and fluoranthene are those presenting the highest emission factors and, consequently, the highest individual PAH annual emissions

at a national level. Emissions of PAHs have been reported to increase with increasing wood combustion temperature. PAHs are mainly formed at combustion temperatures of 700–900ºC (Kjällstrand and Olsson, 2004). These temperature values are reached in modern, efficient combustion devices, but are rarely achieved in traditional appliances, such as those that predominate in Portugal. The total PAH emissions from RWC in Portugal (about 9 t y^{-1}) represent approximately 6.5% of the total emission estimates for the country, according to a recent inventory, in which forest fires were not accounted for and, among the economic sectors, field burning of agricultural wastes and industrial waste incineration were pointed out as the major emitters (Pereira et al., 2011).

Table 8.9 PAH emissions by district (t y^{-1}).

District	**BaA**	**BaP**	**IcdP**	**DBA**	**BFs**	**Ph**	**Flu**	**Pyr**	**C**
Aveiro	0.048	0.040	0.016	0.003	0.058	0.075	0.112	0.175	0.048
Beja	0.017	0.015	0.006	0.001	0.017	0.035	0.049	0.070	0.017
Braga	0.034	0.028	0.012	0.002	0.049	0.058	0.079	0.135	0.035
Bragança	0.027	0.021	0.009	0.002	0.029	0.037	0.051	0.095	0.028
Castelo Branco	0.037	0.033	0.013	0.002	0.039	0.066	0.091	0.142	0.037
Coimbra	0.033	0.022	0.011	0.002	0.038	0.054	0.079	0.118	0.033
Évora	0.011	0.011	0.005	0.001	0.019	0.031	0.038	0.058	0.012
Faro	0.010	0.008	0.003	0.001	0.011	0.020	0.027	0.040	0.010
Guarda	0.012	0.010	0.004	0.001	0.016	0.018	0.028	0.045	0.013
Leiria	0.034	0.025	0.012	0.002	0.043	0.048	0.071	0.127	0.037
Lisboa	0.039	0.033	0.014	0.003	0.053	0.089	0.109	0.179	0.042
Portalegre	0.005	0.004	0.002	0.000	0.007	0.011	0.014	0.023	0.006
Porto	0.049	0.039	0.019	0.003	0.081	0.091	0.113	0.208	0.050
Santarém	0.033	0.025	0.011	0.002	0.038	0.044	0.064	0.116	0.036
Setúbal	0.030	0.028	0.011	0.002	0.033	0.074	0.100	0.138	0.031
Viana do Castelo	0.007	0.005	0.003	0.0005	0.011	0.012	0.016	0.031	0.008
Vila Real	0.013	0.010	0.005	0.001	0.017	0.019	0.028	0.055	0.016
Viseu	0.036	0.027	0.013	0.002	0.045	0.057	0.088	0.139	0.039

BaA – Benzo[a]anthracene
BaP – Benzo[a]pyrene
IcdP – Indeno[1,2,3-cd]pyrene
DBA – Dibenzo[a,h]anthracene
BFs – Benzofluoranthenes
Ph – Phenanthrene
Flu – Fluoranthene
Pyr – Pyrene
C – Chrysene

8.4 Conclusions

Residential wood combustion is one of the largest sources of fine particle emissions to the atmosphere in Portugal. Since wood burning practices and activities can vary geographically, residential wood combustion chemical composition profiles also differ by region. An assessment of RWC practices was made through a national scale survey. The survey was based on 2387 effective respondents, from which a total of 806 positive answers were obtained, i.e., house owners who have declared the use of RWC. The total amount of wood consumed in Portugal in the year 2010 was 1.95 Mt for both heating (83%) and cooking (17%) purposes. In the households where wood is frequently burned, 43% use fireplaces, while 6% of respondents said that burn wood in barbecue fireplaces. Traditional stoves and closed fireplaces represent about 44% of the total number of appliances. The percentage penetration for pellet stoves and other innovative appliances is about 7%. Regarding wood species used, Holm oak and cork oak are the most common woods for residential combustion in the southern districts; maritime pine, Portuguese oak and eucalypt present a larger share in northern districts. Around 20% of the house owners burn mixtures of different types of woods. The use of different appliances and wood species is of great importance because both affect the amount and type of emissions ($PM_{2.5}$, OC, EC and organic compounds).

The information obtained with the survey combined with the databases on emission factors from the laboratory burning tests allowed us to estimate the pollutant amounts emitted in each Portuguese district. The emissions of $PM_{2.5}$ were estimated to be between 0.09 kt y^{-1} (Portalegre) and 1.30 kt y^{-1} (Aveiro), totalising 10.96 kt y^{-1} in Portugal. The national emissions of OC and EC were estimated to be 5.32 and 0.53 kt y^{-1}, respectively. It was estimated that the total CO_2 emissions from RWC in Portugal are 1.7 Mt y^{-1}. The levoglucosan emissions contribute with between 7.8% (Beja) and 16.1% (Vila Real) of $PM_{2.5}$ emissions from RWC. PAHs from RWC in Portugal represent approximately 6.5% of the total emissions from the main activity sectors.

Taking into account that $PM_{2.5}$ emissions from RWC represent 30% of the global emissions from several activity sectors, regular updates of inventories are required. The assessment of how much emission estimates will change as a result of the adoption of abatement strategies, and consequently, how much the ambient $PM_{2.5}$ (and their constituents) levels will reduce is also highly recommended.

Acknowledgements

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CHAPTER 9

Chapter 9. General Conclusions

The research described in this thesis enabled significant advances in the field of biomass burning emissions in Portugal, contributing to bridge the information gap on both gaseous and particulate compounds from one that is among the largest sources of pollutants. The emissions from (i) residential wood combustion, (ii) field burning of garden and agriculture residues and (ii) forest fires were extensively characterised in this research. Regarding the residential wood combustion, different biomass types (the most commonly used in Portugal) and equipments (traditional versus modern; closed versus open) were studied. Burning tests with different temperatures (cold start versus hot start) were performed and particulate matter with different sizes (PM_{10} and $PM_{2.5}$) was collected. Emissions from the open burning of garden and agriculture wastes were also selected for this study, because this represents a common method of disposal for this specific type of garbage, especially in certain periods of the year, and the biomass is very different from the one used in residential combustion. Wildfires are amongst the most damaging factors in Mediterranean countries and they are progressively becoming a major source of air pollutants. However, due to the uncontrolled and dangerous nature of wildfires, emissions were obtained from prescribed fires. Data obtained with the household biomass consumption survey, combined with the databases of emission factors from the laboratory tests, allowed the estimation of the global pollutant amounts emitted in Portugal.

The major findings of this study are summarised as follows:

- Concerning residential wood combustion, the traditional Portuguese burning appliances tested in this study present higher $PM_{2.5}$ emission factor, a lower EC content of the fine particle mass, and a higher OC mass fraction, compared to those obtained for the PM_{10} emissions from a modern woodstove. Particle emissions and their OC content from traditional burning appliances are also higher than those described in the literature for the residential wood combustion in countries where certification of combustion equipments is required to meet specific emission limits. In this study, the $PM_{2.5}$ emissions were, on average, higher for the fireplace than for the woodstove. More than 80% of the smoke particle mass was composed of organic matter, while water-soluble ions and trace elements represented a small fraction, with variable contributions, depending on the burning

experiment. This overwhelming proportion of carbonaceous constituents in smoke particles from the low-temperature combustion equipments of this study differs from the fly ash composition of modern appliances with improved combustion conditions, good burn out and low emissions of PM, in which inorganic salts dominate.

Regardless of the biofuel used, equipments, particle size and temperature of combustion, the major organic components in particles from biomass burning were monosaccharide derivatives, in particular levoglucosan, acids and aliphatic compounds. In general, the monosaccharide derivatives allow the distinction between hard- and softwood, taking into account the levoglucosan/mannosan ratio. The dominant aromatic hydrocarbon found in the softwood smoke was retene, whilst it was present at very small levels in the hardwood combustion emissions. Other organic tracers common in RWC emissions were guaiacyl, like vanillic acid, and synapyl compounds. They were identified in softwood smoke, whereas hardwood burning contributed mainly to the formation of syringyl compounds, such as syringic acid. Stigmasterol was only present in the smoke of hardwood species; thus, this compound may be pointed out as a potential tracer for smoke from deciduous trees. β-Sitosterol had a greater expression in the smoke of softwood species. However, as β-sitosterol emissions vary greatly with wood species, it cannot be regarded as a candidate to separate quantitatively hardwood from softwood combustion emissions in source apportionment studies. The application of cluster analysis to the individual smoke composition, indicated that emissions from the cork and Holm oak combustion, whether in the fireplace or in the woodstove, can be grouped into the same composite source profile, while those from the Portuguese oak should be separated into another profile, which also may include the emissions from eucalypts. Emissions from the maritime pine combustion, in both types of appliances, may also be averaged to obtain a single profile.

- The smoke from garden and agriculture residue burning presented $PM_{>10}$ concentrations significantly higher when compared to fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) fractions for three types of biofuels. Probably, due to the high relative humidity conditions during sampling, the formation of larger particles from fog processing, may have occurred. The carbonaceous fraction was dominated by organic carbon (OC/TC~98%). Despite the distribution patterns of organic compounds in PM varied among residues, the amounts of phenolics (predominantly polyphenol and guaiacyl derivatives) and organic acids were always predominant over other organic compounds in the organosoluble fraction of smoke.

PAHs molecular diagnostic ratios were similar to those published for smoke from other agriculture residues, and were different from those reported for other combustion sources, indicating that they can be applied as a source apportionment tool. Biomarkers, such as levoglucosan, *β*-sitosterol and phytol, were detected in appreciable amounts in the smoke of all agricultural/garden residues. In addition, inositol may be considered as an eventual tracer for the potato haulm burning smoke.

- Emissions from forest fires depend on several variables, including the type of species burned, geographical location and geomorphology, meteorological conditions, etc. Thus, emissions should be reported as only indicative of particular conditions. In the description of particulate organic compounds, gases and inorganic compounds, emitted from Mediterranean shrubland wildland fires, resulting from this work, it was concluded that approximately 50% of the particulate mass is constituted by organic carbon. The OC concentrations were 46-fold higher in $PM_{2.5}$ than in $PM_{2.5-10}$, because emissions were dominated by fine particles. The major organic components in particles were triterpenoids with the oleanane and ursane skeletons, steradienes and steratrienes, including unaltered biological precursors (biomolecules) and their degradation products (pyrolysates). Aliphatic lipids (*n*-alkanoic acids, *n*-alkenoic acids, *n*-alkanols and *n*-alkanes), and anhydrosugars (levoglucosan and its stereoisomers) constituted another large fraction of OC. Consistent with the predominance of angiosperms in the forest, syringyl-type phenols from lignin pyrolysis were emitted in higher proportion than guaiacyl-type phenols. Polycyclic aromatic hydrocarbons were also present as minor constituents. More than 30 trace metals and water-soluble ions have been determined in smoke aerosols, representing in total an average contribution of about 7% to the PM_{10} mass. As for gaseous pollutants, emissions of CO_2 and NMHC from these controlled fires, with markedly flaming characteristics, were higher than those reported for fires in other biome types.

- Based on a detailed analysis of the survey carried out to assess the RWC practices in Portugal, it was estimated that the total amount of wood consumed in the past year of 2010 was 1.95 Mt for both heating (83%) and cooking (17%) purposes. Regarding to wood species used, Holm oak and cork oak are the most common woods for residential combustion in the southern districts. Maritime pine, Portuguese oak and eucalypt present a larger share in northern districts. The emissions of $PM_{2.5}$ from RWC were determined to be 10.96 kt y^{-1}, representing 30% of the estimate for different source activities. The global

national emissions of OC and EC were estimated to be 5.32 and 0.53 kt y^{-1}, respectively. It was also estimated that, in Portugal, the total CO_2 emissions from RWC are close to 1 Mt y^{-1}. The levoglucosan emissions contribute with 7.8% to 16.1% of $PM_{2.5}$ emissions from RWC. This detailed information gives a more realistic idea of what's happening in Portugal in terms of biomass consumption and related emissions.

Data obtained in this study can contribute to the improvement of existing emission inventories and can be applied in receptor models to assess the contribution of biomass burning to the levels of atmospheric aerosols and their constituents obtained in monitoring campaigns in Southern Europe.

Presently, efforts to reduce particulate matter pollution tend to focus on fossil fuels. However, it has been demonstrated that, in Portugal and other European countries, in addition to vehicular emissions, RWC can significantly contribute to surmount the limit values set out for PM_{10} or $PM_{2.5}$ in the Directive 2008/50/EC of the European Parliament. Air quality management plans should address this source of emissions throughout Europe, using a combination of legislation and technological advances, in order to cut pollution. In Portugal, a real commitment on the certification process of burning equipments must be reached. On the other hand, the use of catalytic elements in the woodstove designs or high-efficiency woodstoves that reduce emissions by careful control of air flow and temperature should become a common practice.

The comparison of emissions from this study with literature data showed significant differences between the various types of combustion equipments, especially old-type residential appliances versus modern woodstoves and boilers with higher combustion efficiency. More detailed characterisation of the variations in particle properties between the different types of appliances is however still wanted, taking into account the vast array of technologies and models existent. It is desirable to extend the combustion tests for different species from other Mediterranean countries and also to other types of garden and agriculture residues, to use correctly the profiles of biomass burning emissions in source attribution studies.

The comprehensive chemical characterisation data sets obtained in these experiments are potentially very useful for numerical models that evaluate the impact of biomass burning on the microscale to regional-scale atmosphere in the Mediterranean region. Taking into account that, in addition to emission inventories, climate change,

atmospheric photochemical and source apportionment, models use emission profiles which should reflect the regional characteristics of biofuels, and that considerable uncertainties remain regarding the magnitude of carbon exchanges between the wildland burning and the atmosphere, it has yet to be estimated more specific and representative emission profiles for wildfires in wood-dominated forests in Southern Europe, especially under extreme weather conditions.

Supplementary Material

Supplementary Material A1

The concentrations of all organic compounds from Chapter 2.

Table A1. Detailed speciation of organic compounds in wood smoke (mg g^{-1} OC).

Compound	Formula	*Eucalyptus globulus*	*Pinus pinaster*	*Quercus suber*	*Acacia longifolia*
***n*-Alkanes**					
Tetradecane	$C_{14}H_{30}$	0.00176	---	+	0.0148
Pentadecane	$C_{15}H_{32}$	0.169	0.0747	0.00913	0.267
Hexadecane	$C_{16}H_{34}$	0.0123	0.0875	0.00253	0.0159
Heptadecane	$C_{17}H_{36}$	0.0540	0.0974	0.00717	0.0331
Pristane	$C_{19}H_{40}$	0.0173	0.00156	0.00292	0.0400
Octadecane	$C_{18}H_{38}$	0.109	---	+	0.0600
Nonadecane	$C_{19}H_{40}$	0.156	0.0231	0.0117	0.0556
Eicosane	$C_{20}H_{42}$	0.132	0.0409	---	0.128
Heneicosane	$C_{21}H_{44}$	0.323	0.122	0.00570	0.415
Docosane	$C_{22}H_{46}$	0.794	0.244	0.153	0.854
Tricosane	$C_{23}H_{48}$	0.670	0.376	0.0104	0.576
Tetracosane	$C_{24}H_{50}$	1.19	0.557	0.187	1.22
Pentacosane	$C_{25}H_{52}$	1.11	0.664	0.0525	0.450
Hexacosane	$C_{26}H_{54}$	1.28	1.13	0.0970	0.835
Heptacosane	$C_{27}H_{56}$	1.53	1.82	0.0502	0.827
Octacosane	$C_{28}H_{58}$	1.59	1.86	0.0670	2.51
Nonacosane	$C_{29}H_{60}$	1.78	2.22	0.0903	0.897
Hentriacontane	$C_{31}H_{64}$	1.74	2.54	0.123	0.850
Dotriacontane	$C_{32}H_{66}$	1.69	2.52	0.123	1.08
Tritriacontane	$C_{33}H_{68}$	1.57	2.53	0.110	0.875
Tetratriacontane	$C_{34}H_{70}$	1.24	2.00	0.0978	0.713
Other Alkanes		12.1	8.37	2.31	6.90
Total Alkanes		**29.2**	**27.1**	**3.51**	**19.6**
***n*-Alkenes**					
Tetradecene	$C_{14}H_{28}$	0.0900	0.0419	0.00315	0.0755
Pentadecene	$C_{15}H_{30}$	0.0100	---	---	---
Hexadecene	$C_{16}H_{32}$	0.0451	0.0353	0.0404	---
Octadecene	$C_{18}H_{36}$	0.0417	0.0190	0.0101	0.110
Nonadecene	$C_{19}H_{38}$	0.170	0.0480	0.00321	0.0367
Eicosene	$C_{20}H_{40}$	0.104	0.0915	0.0113	---
Heneicosene	$C_{21}H_{42}$	0.151	7.28	0.410	4.53
Docosene	$C_{22}H_{44}$	0.102	0.101	0.0439	0.579
cis-9-Tricosene	$C_{23}H_{46}$	0.845	0.648	0.286	0.659

Tetracosene	$C_{24}H_{48}$	0.182	0.184	0.159	1.35
Pentacosene	$C_{25}H_{50}$	0.0484	---	0.0307	0.504
Hexacosene	$C_{26}H_{52}$	0.152	0.0636	0.00154	14.5
Octacosene	$C_{28}H_{54}$	0.0512	---	---	---
Nonacosene	$C_{29}H_{56}$	0.0800	---	0.100	1.13
Other Alkenes		1.79	0.0545	0.115	0.245
Total Alkenes		**3.87**	**8.57**	**1.21**	**23.7**
PAH					
Naphthalene	$C_{10}H_8$	0.0323	0.136	0.00351	0.0579
Acenaphthylene	$C_{12}H_8$	+	0.00497	+	+
Acenaphthene	$C_{12}H_{10}$	0.00446	0.000574	+	0.00235
Fluorene	$C_{13}H_{10}$	+	0.00368	+	+
Phenanthrene	$C_{14}H_{10}$	0.0383	1.75	0.118	0.00693
Anthracene	$C_{14}H_{10}$	0.00104	0.316	0.301	+
Fluoranthene	$C_{16}H_{10}$	1.45	14.7	2.84	1.20
Pyrene	$C_{16}H_{10}$	1.40	8.10	0.811	1.04
p-terphenyl	$C_{18}H_{14}$	0.0109	0.125	0.0111	0.0216
Retene	$C_{18}H_{18}$	0.147	14.3	0.141	0.155
Benzo[a]anthracene	$C_{18}H_{12}$	0.424	6.21	0.182	0.629
Chrysene	$C_{18}H_{12}$	0.661	8.88	0.260	1.00
Benzo[b]fluoranthene	$C_{20}H_{12}$	0.232	6.16	0.0870	0.617
Benzo[k]fluoranthene	$C_{20}H_{12}$	0.285	2.90	0.354	0.786
Benzo[a]pyrene	$C_{20}H_{12}$	0.336	5.28	0.0917	0.431
Perylene	$C_{20}H_{12}$	0.0626	0.875	0.0155	0.0851
Indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	0.272	3.84	0.0395	0.761
Dibenzo[a,h]anthracene	$C_{24}H_{14}$	0.0293	0.588	0.00955	0.0713
Benzo[ghi]perylene	$C_{22}H_{12}$	0.207	7.26	0.374	1.98
Benzo[j]fluoranthene	$C_{20}H_{12}$	0.239	3.92	0.0693	0.424
Benzo[e]pyrene	$C_{20}H_{12}$	0.295	4.59	0.0730	0.540
Other PAHs		14.0	70.1	42.0	21.5
Total PAHs		**20.1**	**160**	**47.8**	**31.3**
Oxygenated aromatics					
9(10H)-Anthracenone	$C_{14}H_8O_2$	---	0.384	0.101	---
9H-Xanthen-9-one	$C_{13}H_8O_2$	0.816	0.979	0.547	2.87
9,10-Anthracenedione	$C_{14}H_8O_2$	0.325	3.33	0.463	0.0284
Cyclopenta(def)phenanthrenone	$C_{15}H_8O$	0.435	0.560	0.808	0.970
7H-Benz[de]anthracen-7-one	$C_{17}H_{10}O$	0.115	2.45	0.0444	8.70
Benz[a]anthracene-7,12-dione	$C_{18}H_{10}O_2$	---	1.52	---	0.873
9-Fluorenone	$C_{13}H_8O$	0.806	4.10	1.04	3.02
2,6-di-*tert*-butil-1,4-benzoquinone	$C_{14}H_{20}O_2$	0.000476	0.0113	0.0268	0.0261
***n*-Alkanals**					
Decanal	$C_{10}H_{20}O$	0.0460	0.0345	0.0632	0.0491
Hexadecanal	$C_{16}H_{32}O$	0.0621	---	---	---
Ketones					

2-Tridecanone	$C_{13}H_{26}O$	0.00250	---	0.00384	0.00278
2-Pentadecanone	$C_{15}H_{30}O$	0.00269	0.00282	0.00199	0.00303
3-Hexadecanone	$C_{16}H_{32}O$	0.00366	0.00730	0.00507	0.0246
2-Octadecanone	$C_{18}H_{36}O$	0.00800	0.00833	0.00723	0.0397
2-Pentadecanone, 6,10,14-trimethyl-	$C_{18}H_{38}O$	0.0531	---	---	0.101
Triterpenoids					
β-Amyrin	$C_{30}H_{50}O$	4.83	0.183	1.57	---
Urs-12-en-one (α-amyrenone)	$C_{30}H_{48}O$	0.499	0.0870	0.0400	0.0839
Lupeol	$C_{30}H_{50}O$	0.132	0.00520	1.05	0.662
3-Keto-urs-12-ene	$C_{30}H_{48}O$	0.321	---	0.0592	---
4-Cholesten-3-one	$C_{27}H_{44}O$	0.0533	0.0500	0.0538	0.0179
Cholest-4-ene, 3-methoxy-, (3-β)-	$C_{28}H_{48}O$	0.734	---	2.12	---
3-aza-A-homocholest-4a-en-4-one	$C_{27}H_{45}NO$	5.40	---	1.71	---
Terpenoids					
Verbenone	$C_{10}H_{14}O$	---	---	1.66	2.90
Eucalyptol	$C_{10}H_{18}O$	0.100	0.0237	0.0111	0.0166
(S)-(-)-β-Citronellol	$C_{10}H_{20}O$	---	---	0.00111	0.201
(-)-Isopulegol	$C_{10}H_{18}O$	---	0.0165	0.112	0.0730
(1S,2S,3R,5S) -(+)-2,3-Pinanediol	$C_{10}H_{18}O_2$	0.0860	0.0176	0.308	0.0395
Phenolic compounds					
4-Octylphenol	$C_{14}H_{22}O$	0.0367	0.0309	0.106	0.138
cis-2-Methylcyclohexanol	$C_7H_{14}O$	---	0.0130	0.00478	---
Vanillic acid	$C_8H_8O_4$	4.93	15.0	6.95	11.5
Syringic acid	$C_9H_{10}O_5$	35.4	1.75	27.9	26.3
Sinapic acid	$C_{11}H_{12}O_5$	0.410	0.0371	0.322	0.128
Vanillin	C_8H_8O	4.29	0.387	12.1	1.80
Coniferyl aldehyde	$C_{10}H_{10}O_3$	0.00258	0.0145	0.0183	0.0581
Syringaldehyde	$C_9H_{10}O_4$	0.00535	0.00184	0.0227	0.0122
Coniferyl alcohol	$C_{10}H_{12}O_3$	0.0411	0.101	3.92	0.276
Sinapyl alcohol	$C_{11}H_{14}O_4$	0.0299	0.0176	0.505	0.0120
Vitamin E acetate	$C_{31}H_{52}O_3$	0.302	0.553	0.0815	---
(±)-α-Tocopherol (Vitamin E)	$C_{29}H_{50}O_2$	0.0316	---	0.0109	---
Total phenolic compounds		**45.5**	**17.9**	**51.9**	**40.2**
***n*-Alcohols**					
n-Heptanol	$C_7H_{16}O$	---	---	5.04	---
n-Decanol	$C_{10}H_{22}O$	0.583	0.475	1.22	0.544
n-Pentadecanol	$C_{15}H_{32}O$	0.0427	0.0355	0.0240	0.0351
n-Hexadecanol	$C_{16}H_{34}O$	---	---	---	0.288
n-Octadecanol	$C_{18}H_{38}O$	17.5	1.83	1.20	3.74
n-Docosanol	$C_{20}H_{42}O$	1.06	0.716	2.08	0.714
n-Tricosanol	$C_{23}H_{48}O$	0.109	---	0.0733	---
n-Pentacosanol	$C_{25}H_{52}O$	0.368	0.0459	0.330	0.0976
n-Heptacosanol	$C_{27}H_{56}O$	0.201	0.0176	0.11	---
n-Octacosanol	$C_{28}H_{58}O$	0.469	0.159	---	2.94
n-Tricontanol	$C_{30}H_{62}O$	0.122	---	---	---

Other Alcohols		68.8	19.9	220	8.55
Total alcohols		**89.3**	**23.1**	**230**	**16.9**
Phytosterols and derivatives					
β-Sitosterol	$C_{29}H_{50}O$	15.8	7.33	14.7	0.890
Stigmasterol	$C_{29}H_{48}O$	0.480	---	0.238	0.571
Stigmasta-3,5-dien-7-one	$C_{29}H_{46}O$	---	---	0.181	---
Stigmast-4-en-3-one	$C_{29}H_{48}O$	---	---	0.537	---
***n*-alkanoic acids**					
Octanoic acid	$C_8H_{16}O_2$	0.0448	0.0589	0.0153	0.0465
Nonanoic acid	$C_9H_{18}O_2$	0.0884	0.166	0.0484	0.0639
Decanoic acid	$C_{10}H_{20}O_2$	0.138	0.165	0.0361	0.112
Undecanoic acid	$C_{11}H_{22}O_2$	0.579	0.186	0.447	0.523
Dodecanoic Acid	$C_{12}H_{24}O_2$	0.412	0.0785	0.145	0.0909
Tridecanoic acid	$C_{13}H_{26}O_2$	0.104	0.135	0.0424	0.454
Tetradecanoic acid	$C_{14}H_{28}O_2$	1.34	1.45	0.684	3.30
Pentadecanoic acid	$C_{15}H_{30}O_2$	0.396	0.787	0.326	2.42
Hexadecanoic acid	$C_{16}H_{32}O_2$	13.5	6.29	3.83	18.6
Heptadecanoic acid	$C_{17}H_{34}O_2$	0.199	0.416	0.276	1.24
Octadecanoic acid	$C_{18}H_{36}O_2$	8.99	2.96	0.621	8.14
Nonadecanoic acid	$C_{19}H_{38}O_2$	0.206	0.309	0.111	0.727
Eicosanoic acid	$C_{20}H_{40}O_2$	0.769	3.71	0.321	2.85
Docosanoic acid	$C_{22}H_{44}O_2$	1.97	11.6	1.06	15.2
Tetracosanoic acid	$C_{24}H_{48}O_2$	2.80	9.81	0.969	17.5
Total n-alkanois acids		**31.5**	**38.1**	**8.93**	**71.2**
***n*-di-acids**					
Propanedioic acid	$C_3H_4O_4$	2.50	2.01	0.160	0.574
Butanedioic acid	$C_4H_6O_4$	5.46	2.47	2.09	1.43
Pentanedioic acid	$C_5H_8O_4$	3.50	1.55	1.04	0.793
Hexanedioic acid	$C_6H_{10}O_4$	0.315	0.371	0.099	0.306
Heptanedioic acid	$C_7H_{12}O_4$	8.04	3.31	5.93	6.23
Octanedioic acid	$C_8H_{14}O_4$	1.95	1.43	0.674	1.78
Nonanedioic acid	$C_9H_{16}O_4$	0.399	0.946	0.286	1.69
Decanedioic acid	$C_{10}H_{18}O_4$	0.0805	0.139	0.0704	0.320
Hexadecanedioic acid	$C_{16}H_{30}O_4$	0.102	0.195	0.0941	1.23
Resin acids					
Isopimaric acid	$C_{20}H_{30}O_2$	0.215	31.2	0.198	0.706
Pimaric acid	$C_{20}H_{30}O_2$	---	4.70	---	---
Abietic acid	$C_{20}H_{30}O_2$	0.235	1.50	0.293	0.363
Dehydroabietic acid	$C_{20}H_{28}O_2$	0.142	5.44	0.103	---
Unsaturated acids					
Linoleic acid ($C_{18:2}$)	$C_{18}H_{32}O_2$	5.53	0.579	3.09	3.76
Other acids		248	649	144	310
Total acids		308	743	167	401

Alkyl ester acids					
Tetradecanoic acid, 1-methylethyl ester	$C_{17}H_{34}O_2$	0.312	0.304	0.0494	0.167
Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$	0.115	0.387	0.262	0.653
Octadecanoic acid, methyl ester	$C_{18}H_{38}O_2$	0.147	1.34	0.742	0.0680
Hexanedioic acid, dioctyl ester	$C_{22}H_{42}O_4$	0.605	4.31	0.332	0.393
Docosanoic acid, methyl ester	$C_{23}H_{46}O_2$	0.251	0.178	0.761	---
Tricosanoic acid, methyl ester	$C_{24}H_{48}O_2$	0.0394	---	0.149	0.139
Tetracosanoic acid, methyl ester	$C_{25}H_{50}O_2$	0.173	---	0.263	---
Octanoic acid, 1,2,3-propanetriyl ester	$C_{27}H_{50}O_6$	0.429	1.00	0.118	0.115
Tetradecanoic acid, tetradecyl ester	$C_{28}H_{56}O_2$	0.0614	0.390	0.221	---

(---) not detected; (+) detected, but not quantified, because of abundances close to the detection limit.

Supplementary Material A2

The concentrations of all organic compounds from Chapter 3.

Table A2. Detailed speciation of organic compounds in wood smoke (mg g^{-1} OC).

Compounds	Formula	Maritime pine				Golden wattle				Holm oak				Eucalypt			
		W_Hot	W_Cold	F_Hot	F_Cold	W_Hot	W_Cold	F_Hot	F_Cold	W_Hot	W_Cold	F_Hot	F_Cold	W_Hot	W_Cold	F_Hot	F_Cold
***n*-Alkanes**																	
Tetradecane[a]	$C_{14}H_{30}$	0.632	---	0.250	0.152	0.0374	---	0.0263	0.159	0.0751	---	---	0.0179	0.0468	---	0.0428	---
Pentadecane[a]	$C_{15}H_{32}$	---	---	---	0.130	---	---	---	0.0983	---	---	---	---	---	---	---	---
Hexadecane[a]	$C_{16}H_{34}$	---	---	0.0629	0.0928	0.0120	---	---	0.0551	0.0376	---	---	---	0.0227	---	0.0228	---
Heptadecane[a]	$C_{17}H_{36}$	0.154	+	0.0131	0.0499	+	0.00198	0.00601	0.0461	+	0.00367	+	0.00375	+	+	0.000550	+
Octadecane[a]	$C_{18}H_{38}$	0.0607	+	0.0192	+	+	+	0.0143	0.00389	0.00828	+	+		0.0152	+	0.00783	+
Pristane[a]	$C_{19}H_{40}$	---	---	0.00740	---	---	---	---	---	0.00934	---	---	---	0.00283	---	---	---
Nonadecane[a]	$C_{19}H_{40}$	---	---	---	0.0190	0.0123	---	---	0.0246	0.0453	---	---	0.00660	0.0158	---	---	---
Eicosane[a]	$C_{20}H_{42}$	0.0638	+	0.0229	0.0130	0.0223	0.0286	0.0167	0.0559	0.0306	0.00803	0.00293	0.0108	0.0108	0.000985	+	+
Heneicosane[a]	$C_{21}H_{44}$	0.111	+	0.0257	0.0233	0.0594	0.108	0.0361	0.195	0.0380	0.00955	0.00761	0.0233	0.0162	+	0.000837	+
Docosane[a]	$C_{22}H_{46}$	0.524	+	0.0506	0.00137	+	0.195	0.0459	0.405	+	+	0.0139	0.0146	+	+	+	+
Tricosane[a]	$C_{23}H_{48}$	1.76	+	0.189	0.0886	+	0.438	0.187	0.999	+	+	0.0803	0.0695	+	+	0.0733	0.0178
Tetracosane[a]	$C_{24}H_{50}$	3.57	+	+	+	+	0.774	+	1.72	+	+	0.0762	+	+	+	+	+
Pentacosane[a]	$C_{25}H_{52}$	6.82	+	+	+	+	1.11	+	2.36	+	+	0.182	+	+	+	+	+
Hexacosane[a]	$C_{26}H_{54}$	10.4	+	+	+	+	1.55	0.102	2.70	+	+	0.258	+	+	+	+	+
Heptacosane[a]	$C_{27}H_{56}$	12.1	+	0.0791	+	+	1.63	0.202	2.88	+	+	0.328	0.0400	+	+	+	+
Octacosane[a]	$C_{28}H_{58}$	12.2	+	0.118	+	+	1.74	0.310	2.43	+	+	0.327	0.0911	+	+	+	+
Nonacosane[a]	$C_{29}H_{60}$	10.1	+	0.187	+	+	0.895	0.294	1.95	+	+	0.267	0.0950	+	+	+	+
Triacontane[a]	$C_{30}H_{62}$	9.12	+	0.329	+	+	0.832	0.377	1.74	+	+	0.259	0.0514	+	+	0.0246	+
Hentriacontane[a]	$C_{31}H_{64}$	5.09	+	0.312	+	+	0.189	0.251	0.839	+	+	0.144	0.103	+	+	0.0960	+
Dotriacontane[a]	$C_{32}H_{66}$	3.27	+	0.163	0.0535	+	+	0.160	0.490	+	+	0.0705	0.0435	+	+	0.00364	+
Tritriacontane[a]	$C_{33}H_{68}$	1.76	+	0.109	0.0979	+	0.0308	0.103	0.240	+	+	0.0335	0.0353	+	+	0.0106	+
Tetratriacontane[a]	$C_{34}H_{70}$	0.605	0.00309	0.0788	---	+	0.000206	0.0622	0.103	+	+	0.0153	0.0274	+	+	0.0218	---

Total *n*-Alkanes identified		**78.2**	**0.00309**	**2.01**	**0.721**	**0.143**	**9.52**	**2.19**	**19.5**	**0.244**	**0.0212**	**2.06**	**0.633**	**0.130**	**0.000985**	**0.305**	**0.0178**
$C_{max.}$		**C_{28}**	**C_{34}**	**C_{30}**	**C_{14}**	**C_{21}**	**C_{28}**	**C_{30}**	**C_{27}**	**C_{14}**	**C_{21}**	**C_{27}**	**C_{31}**	**C_{14}**	**C_{20}**	**C_{31}**	**C_{23}**
Total other Alkanes		**6.99**	**3.12**	**0.597**	**3.79**	**1.97**	**7.02**	**1.54**	**4.01**	**2.18**	**2.01**	**0.976**	**1.34**	**0.813**	**0.626**	**2.88**	**3.96**
Σ Alkanes		**85.2**	**3.13**	**2.61**	**4.51**	**2.11**	**16.5**	**3.74**	**23.5**	**2.43**	**2.03**	**3.04**	**1.97**	**0.943**	**0.627**	**3.18**	**3.98**
***n*-Alkenes**																	
Hexadecene[a]	$C_{16}H_{32}$	---	---	0.155	---	0.0456	---	0.0498	---	0.155	---	---	---	0.0381	---	0.0227	---
Octadecene[a]	$C_{18}H_{36}$	0.121	+	0.0592	+	0.0251	+	0.0493	0.0124	0.0971	+	+	0.00752	0.0273	+	0.00121	+
Nonadecene[a]	$C_{19}H_{38}$	---	---	---	---	0.0269	---	---	---	---	---	---	---	---	---	---	---
Eicosene[a]	$C_{20}H_{40}$	0.0818	0.0150	0.0363	0.0530	0.133	0.0540	0.0405	0.0535	0.145	0.0165	0.0127	0.0356	0.0474	0.00852	0.00131	+
Heneicosene[a]	$C_{21}H_{42}$	---	0.0137	+	+	0.162	0.0860	0.0334	0.0996	0.0871	0.0285	0.0148	0.0459	0.0350	0.00978	0.00319	+
Docosene[a]	$C_{22}H_{44}$	---	0.0248	0.0456	+	0.188	0.107	0.0715	0.143	0.249	0.0536	0.0523	0.143	0.107	0.0130	+	0.000828
cis-9-Tricosene[a]	$C_{23}H_{46}$	---	---	+	+	0.141	0.0904	+	0.0627	0.111	0.0239	+	+	0.0455	0.0119	+	+
Tetracosene[a]	$C_{24}H_{48}$	---	0.0350	0.0679	---	0.613	0.383	0.105	0.649	0.279	0.0537	0.0192	0.141	0.114	0.0158	0.0193	0.00654
Pentacosene[a]	$C_{25}H_{50}$	---	---	---	---	0.0597	---	---	---	0.0436	---	---	0.0220	0.0216	---	---	---
Hexacosene[a]	$C_{26}H_{52}$	---	---	---	---	0.689	0.526	0.0867	1.13	0.168	---	---	---	0.148	---	---	---
Octacosene[a]	$C_{28}H_{54}$	---	---	---	---	0.341	---	---	0.784	---	---	---	---	---	---	---	---
Total *n*-Alkenes identified		**0.203**	**0.0884**	**0.364**	**0.0530**	**2.42**	**1.25**	**0.436**	**2.94**	**1.33**	**0.176**	**0.099**	**0.395**	**0.583**	**0.0590**	**0.0478**	**0.00736**
$C_{max.}$		**C_{18}**	**C_{24}**	**C_{16}**	**C_{20}**	**C_{26}**	**C_{26}**	**C_{24}**	**C_{26}**	**C_{24}**	**C_{24}**	**C_{22}**	**C_{22}**	**C_{26}**	**C_{24}**	**C_{16}**	**C_{24}**
Total other Alkenes		**1.37**	**0.549**	**0.0291**	**0.137**	**0.408**	**1.22**	**0.0876**	**0.374**	**0.267**	**0.224**	**0.0626**	**0.353**	**0.0617**	**0.0789**	**0.128**	**0.593**
Σ Alkenes		**1.57**	**0.637**	**0.393**	**0.190**	**2.83**	**2.47**	**0.524**	**3.31**	**1.60**	**0.400**	**0.162**	**0.748**	**0.645**	**0.138**	**0.176**	**0.600**
PAHs																	
Naphthalene[a]	$C_{10}H_8$	0.0145	0.0151	---	0.0244	0.00370	0.0275	0.0105	0.0107	0.00158	0.0182	0.000358	0.000118	0.000537	0.0000892	0.000527	0.00612
Acenaphthylene[a]	$C_{12}H_8$	---	0.000279	0.000884	0.00451	0.000543	0.000921	0.00102	0.00300	0.00683	0.00503	0.0244	0.00231	0.00104	0.00711	0.0000523	0.00131

Acenaphthene[a]	$C_{12}H_{10}$	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Fluorene[a]	$C_{13}H_{10}$	---	0.00112	0.00634	0.0125	0.00425	0.00732	0.00276	0.0113	0.0261	0.0154	0.0612	0.00671	0.00218	0.0279	0.000172	0.00242
Phenanthrene[a]	$C_{14}H_{10}$	0.104	0.199	0.0389	0.371	0.165	0.226	0.0696	0.173	0.117	0.397	0.585	0.114	0.0710	0.285	0.00696	0.0886
Anthracene[a]	$C_{14}H_{10}$	0.0411	0.0645	0.0124	0.102	0.0624	0.0852	0.0229	0.0701	0.0417	0.150	0.272	0.0485	0.0271	0.124	0.00264	0.0331
Fluoranthene[a]	$C_{16}H_{10}$	0.231	0.261	0.163	0.414	0.288	0.210	0.362	0.194	0.387	0.420	0.751	0.112	0.183	0.258	0.0419	0.138
Pyrene[a]	$C_{16}H_{10}$	2.50	0.329	0.213	0.575	0.479	0.261	0.385	0.307	0.492	0.545	1.08	0.174	0.217	0.334	0.0517	0.177
p-terphenyl[a]	$C_{18}H_{14}$	---	0.00223	0.00180	0.00401	0.00259	0.00145	0.00202	0.00157	0.00480	0.00332	0.00517	0.00129	0.00150	0.00144	0.000305	0.000752
Retene[a]	$C_{18}H_{18}$	15.4	4.12	1.54	6.43	0.157	0.435	0.283	0.0489	0.153	0.357	0.0229	0.0350	0.103	0.117	+	0.0844
Benzo[a]anthracene[a]	$C_{18}H_{12}$	0.173	0.119	0.0846	0.189	0.0946	0.0794	0.107	0.0768	0.184	0.0649	0.279	0.0394	0.0612	0.109	0.0158	0.0412
Chrysene[a]	$C_{18}H_{12}$	0.366	0.121	0.0850	0.184	0.0992	0.0786	0.107	0.0674	0.203	0.0643	0.222	0.0353	0.0558	0.0754	0.0163	0.0414
Benzo[b]fluoranthene[a]	$C_{20}H_{12}$	---	0.0376	0.0435	0.0829	0.0235	0.0309	0.0397	0.0342	0.0619	0.114	0.113	0.0118	0.0164	0.0703	0.00620	0.0152
Benzo[k]fluoranthene[a]	$C_{20}H_{12}$	---	0.0323	0.0274	0.0523	0.0194	0.0221	0.0269	0.0209	0.0451	0.0632	0.0722	0.0100	0.0143	0.0387	0.00507	0.0148
Benzo[j]fluoranthene[a]	$C_{20}H_{12}$	---	0.0496	0.0368	0.0773	0.0267	0.0306	0.0373	0.0275	0.0676	0.0862	0.0988	0.0142	0.0175	0.0495	0.00675	0.0140
Benzo[a]pyrene[a]	$C_{20}H_{12}$	---	0.0454	0.0703	0.124	0.0464	0.0441	0.0644	0.0511	0.108	0.125	0.171	0.0196	0.0391	0.0811	0.0101	0.0283
Benzo[e]pyrene[a]	$C_{20}H_{12}$	---	0.0381	0.0538	0.0147	0.0392	0.0300	0.0522	0.0375	0.108	0.0888	0.112	0.0133	0.0293	0.0549	0.00894	0.0221
Perylene[a]	$C_{20}H_{12}$	---	0.00846	0.00966	0.0186	0.00702	0.00761	0.00845	0.00714	0.0167	0.0196	0.0226	0.00308	0.00543	0.0131	0.00139	0.00626
Indeno[1,2,3-cd]pyrene[a]	$C_{22}H_{12}$	---	0.0243	0.0465	0.0549	0.0234	0.0243	0.0475	0.0247	0.0506	0.0712	0.0848	0.00908	0.0192	0.0480	0.00639	0.0134
Dibenzo[a,h]anthracene[a]	$C_{24}H_{14}$	---	0.00363	0.00730	0.00827	0.00315	0.00314	0.00588	0.00272	0.00800	0.00848	0.00975	0.00133	0.00200	0.00571	---	---
Benzo[ghi]perylene[a]	$C_{22}H_{12}$	---	0.0159	0.0350	0.0404	0.0174	0.0170	0.0335	0.0169	0.0343	0.0589	0.0644	0.00584	0.0142	0.0423	---	0.0103
Total PAHs identified		**18.8**	**5.48**	**2.48**	**8.78**	**1.56**	**1.62**	**1.67**	**1.19**	**2.12**	**2.68**	**4.05**	**0.657**	**0.881**	**1.74**	**0.181**	**0.739**
Total other PAHs[b]		**10.5**	**17.8**	**8.25**	**18.8**	**3.32**	**4.54**	**4.65**	**3.31**	**3.00**	**2.70**	**3.69**	**3.85**	**1.91**	**1.67**	**1.29**	**7.35**
Σ PAHs		**29.3**	**23.3**	**10.7**	**27.6**	**4.88**	**6.16**	**6.31**	**4.50**	**5.12**	**5.37**	**7.74**	**4.50**	**2.79**	**3.41**	**1.47**	**8.09**
Oxygenated aromatics																	
9-Fluorenone[b]	$C_{13}H_8O$	---	0.0991	0.000436	0.0988	0.0279	0.0671	0.000162	0.0808	---	0.181	0.197	0.0815	0.122	0.106	0.0324	0.0285
9,10-Anthracenedione[b]	$C_{14}H_8O_2$	0.0216	0.0683	0.0408	0.104	0.0318	0.0357	0.0238	0.0585	0.0307	0.0686	0.0821	0.0444	0.0608	0.0333	0.0876	0.0284
2,6-di-tert-butyl-1,4-benzoquinone[b]	$C_{14}H_{20}O_2$	0.119	0.107	0.0248	0.0394	0.0765	0.0308	0.0276	0.0179	0.116	0.0423	0.0555	0.0416	0.0295	0.0157	0.0300	0.0555

Aldehydes[b]		**0.0338**				**0.104**	**0.112**	**0.0100**	**0.107**	**0.245**	**0.0596**	**0.0557**	**0.226**	**0.0768**	**0.0497**		**0.239**
Ketones																	
2-Tridecanone[a]	$C_{13}H_{26}O$	0.0765	0.141	---	0.924	0.0234	0.0596	---	0.128	0.0435	0.0504	---	0.0371	0.00979	0.0485	0.0792	0.120
2-Pentadecanone[a]	$C_{15}H_{30}O$	0.285	0.579	0.167	0.595	0.0919	0.290	0.174	0.133	0.173	0.248	0.362	0.126	0.0582	0.134	0.256	0.00118
3-Hexadecanone[a]	$C_{16}H_{32}O$	0.000758	0.00153	0.000427	0.00199	0.00135	0.00133	0.000886	0.00152	0.00165	0.00189	0.00306	0.00109	0.000632	0.00164	---	---
2-Octadecanone[a]	$C_{18}H_{36}O$	---	---	0.00479	---	0.0188	0.0156	0.00549	0.0119	0.0148	0.0242	0.0242	0.0144	0.0145	---	0.00487	0.399
Total Ketones identified		**0.362**	**0.721**	**0.172**	**1.52**	**0.135**	**0.366**	**0.180**	**0.275**	**0.233**	**0.324**	**0.390**	**0.179**	**0.0831**	**0.184**	**0.340**	**0.520**
Other Ketones[b]		**0.423**	**0.0151**	**0.166**	**0.252**	**0.0537**	**0.0594**	**0.505**	**0.0580**	**0.0550**	**0.0559**	---	**0.0675**	**0.200**	**0.0348**	---	**0.283**
Σ Ketones		**0.786**	**0.736**	**0.338**	**1.77**	**0.189**	**0.426**	**0.685**	**0.333**	**0.288**	**0.380**	**0.390**	**0.246**	**0.283**	**0.219**	**0.340**	**0.804**
Triterpenoids																	
4-Cholesten-3-one[a]	$C_{27}H_{44}O$	---	---	---	---	---	---	---	---	---	0.000141	---	0.0000581	0.000282	0.0000418	0.000260	---
Urs-12-en-one[a]	$C_{30}H_{48}O$	---	---	0.00380	---	0.000914	0.00468	0.000584	0.00673	0.00511	0.00834	0.00101	0.00718	0.0268	---	---	0.000911
Lupeol[a]	$C_{30}H_{50}O$	---	4.73	0.0346	---	0.928	0.442	0.103	0.0129	1.11	0.550	0.0473	0.0596	---	0.00959	---	0.0405
Terpenoids																	
(-)-Isopulegol[a]	$C_{10}H_{18}O$	0.0127	0.00520	0.108	0.0224	0.0110	0.0252	0.0359	0.00707	0.0145	0.0721	0.0439	0.0217	0.0232	0.0258	0.0101	0.0825
(1S,2S,3R,5S) -(+)-2,3-Pinanediol[a]	$C_{10}H_{18}O_2$	0.0796	0.314	0.0238	0.112	2.94	3.50	0.783	0.843	1.22	8.93	6.72	3.72	7.77	5.85	4.65	17.6
Phenolic compounds																	
4-Octylphenol[a]	$C_{14}H_{22}O$	---	0.0399	+	0.00201	0.270	0.351	0.0829	0.178	0.442	0.771	0.475	0.122	0.441	0.469	0.0950	0.336
Vanillic acid[a]	$C_8H_8O_4$	1.72	14.8	0.553	3.46	1.46	3.72	1.68	1.32	1.83	5.45	5.14	2.41	1.02	1.37	1.25	2.94
Syringic acid[a]	$C_9H_{10}O_5$	0.126	0.233	+	0.0665	2.74	2.23	3.91	2.90	8.55	11.4	22.1	9.63	6.73	8.72	12.8	19.2

Sinapic acid[a]	$C_{11}H_{12}O_5$	0.00767	---	---	0.00389	0.0921	0.0548	0.138	0.0586	0.157	0.0874	0.233	0.0818	0.118	0.0613	0.111	0.365
Coniferyl alcohol[a]	$C_{10}H_{12}O_3$	0.0176	0.355	0.759	1.26	0.956	0.946	1.79	3.15	0.583	0.535	7.66	1.13	0.129	0.311	0.143	0.418
Sinapyl alcohol[a]	$C_{11}H_{14}O_4$	---	0.000746	0.00462	---	0.0309	0.0964	0.0198	0.480	0.0455	0.210	0.979	0.214	0.0578	0.132	0.0141	0.207
Catechol[a]	$C_6H_6O_2$	4.21	18.9	2.25	15.0	27.7	23.7	26.0	10.1	25.8	16.8	16.8	19.0	26.1	---	16.7	64.8
Resorcinol[a]	$C_6H_6O_2$	---	0.354	---	---	0.935	0.597	---	0.927	0.432	0.494	1.72	---	1.52	---	1.55	3.22
Methylcatechol[a]	$C_7H_8O_2$	3.38	18.2	3.41	25.3	19.6	29.7	25.8	18.9	12.4	17.6	13.8	10.2	11.1	9.04	9.88	50.6
Pyrogallol[a]	$C_6H_6O_3$	2.22	3.56	0.842	2.73	3.43	29.6	5.73	22.1	5.57	32.7	23.3	38.7	59.2	25.8	70.9	88.9
Vanillin[a]	C_8H_8O	2.59	8.34	3.94	---	5.81	65.2	---	6.47	12.3	5.64	14.0	5.36	3.33	4.90	---	10.8
(±)-α-Tocopherol= Vitamin E[a]	$C_{29}H_{50}O_2$	---	0.113	0.0480	0.0159	0.0230	0.126	0.0548	0.0818	0.386	0.156	1.18	0.199	0.0976	0.0685	0.135	0.314
Other Phenols[b]		24.1	4.89	6.29	0.523	6.13	0.157	4.82	0.310	17.2	0.172	2.29	2.76	5.77	0.123	8.13	5.29
Total phenolic compounds		**38.3**	**69.8**	**18.1**	**48.4**	**69.2**	**157**	**70.0**	**67.0**	**85.6**	**92.0**	**110**	**89.8**	**116**	**51.0**	**122**	**247**
***n*-Alcohols**																	
n-Decanol[a]	$C_{10}H_{22}O$	+	0.00108	0.00449	0.00764	0.00120	0.00519	0.00490	0.00511	0.00407	0.00582	0.0134	0.00389	0.00161	0.00379	0.00184	0.00897
n-Pentadecanol[a]	$C_{15}H_{32}O$	0.000951	0.0108	0.00797	0.0303	0.0489	0.0459	0.00686	0.0757	0.00243	0.00237	0.0424	0.0161	0.00487	0.00513	0.00202	0.00669
n-Octadecanol[a]	$C_{18}H_{38}O$	+	+	0.151	+	0.131	0.000438	0.144	0.405	+	+	0.439	0.0268	0.0190	+	0.0670	0.0928
n-Docosanol[a]	$C_{20}H_{42}O$	0.0353	+	0.409	0.204	0.238	0.223	0.148	0.240	0.685	0.481	2.43	0.382	0.242	0.0163	0.0185	0.506
n-Tricosanol[a]	$C_{23}H_{48}O$	0.00372	0.0142	0.256	0.0670	0.0915	0.148	0.0360	1.10	0.0581	0.0349	0.270	0.0710	0.753	0.0169	0.147	0.156
n-Pentacosanol[a]	$C_{25}H_{52}O$	0.00248	0.0173	0.261	0.0645	0.120	0.275	0.0388	1.39	0.0271	0.0979	0.785	0.228	1.07	0.0309	0.268	0.158
n-Heptacosanol[a]	$C_{27}H_{56}O$	---	---	0.0394	---	---	0.0927	0.0123	0.0588	---	0.00534	---	---	0.0493	0.00834	---	0.0271
n-Octacosanol[a]	$C_{28}H_{58}O$	0.0851	0.00642	0.322	0.00812	2.42	3.72	0.255	1.61	0.0283	0.00832	+	0.00563	0.765	0.0197	0.0132	0.266
n-Tricontanol[a]	$C_{30}H_{62}O$	0.0826	0.00705	0.314	0.00688	0.0153	0.0435	0.00551	0.0202	0.00898	0.0137	0.00918	0.00405	0.600	0.00323	0.00671	0.156
Total *n*-Alkanols identified		**0.210**	**0.0569**	**1.76**	**0.388**	**3.06**	**4.56**	**0.651**	**4.90**	**0.814**	**0.650**	**3.99**	**0.737**	**3.51**	**0.104**	**0.524**	**1.38**
C max.		**C_{28}**	**C_{25}**	**C_{22}**	**C_{22}**	**C_{28}**	**C_{28}**	**C_{28}**	**C_{28}**	**C_{22}**	**C_{22}**	**C_{22}**	**C_{22}**	**C_{25}**	**C_{25}**	**C_{25}**	**C_{22}**
Other Alcohols[b]		**2.21**	**0.115**	**0.00798**	**0.0166**	**4.51**	**1.34**	**0.0144**	**6.42**	**0.0222**	**0.434**	**0.0231**	**0.00607**	**12.0**	**1.27**	**0.0508**	**43.8**

Σ Alcohols		**2.42**	**0.172**	**1.77**	**0.405**	**7.57**	**5.89**	**0.665**	**11.3**	**0.836**	**1.08**	**4.01**	**0.743**	**15.5**	**1.37**	**0.574**	**45.2**
Phytosterols and derivatives																	
Stigmasterol[a]	$C_{29}H_{48}O$	---	---	---	0.0182	0.306	1.19	2.27	1.15	0.212	0.163	0.175	0.309	0.0614	0.0194	0.0238	0.146
β-Sitosterol[a]	$C_{29}H_{50}O$	2.82	5.76	39.9	4.59	1.30	2.83	3.08	1.64	6.01	3.70	5.87	4.71	4.61	3.17	3.15	8.70
Other Phytosterols and derivatives[b]		**0.185**	**1.45**	**0.787**	**0.858**	**0.335**	**1.56**	**0.500**	**0.272**	**2.53**	**0.727**	**0.333**	**0.790**	**1.44**	**1.23**	**0.377**	**1.81**
***n*-Alkanoic Acids**																	
Octanoic acid[a]	$C_8H_{16}O_2$	0.0185	0.0228	+	0.0144	0.0772	0.0349	0.0526	0.0138	0.0334	0.0302	0.0612	0.0151	0.0242	0.00862	0.0109	0.0429
Nonanoic acid[a]	$C_9H_{18}O_2$	0.0237	0.0345	+	+	0.0577	0.0505	0.0289	0.0120	0.0462	0.0497	0.0476	0.0128	0.0286	0.0235	+	0.0300
Decanoic acid[a]	$C_{10}H_{20}O_2$	0.0263	0.0350	+	0.0217	0.0512	0.0625	0.0194	+	0.0427	0.0640	0.101	0.0333	0.0260	---	+	0.0359
Undecanoic acid[a]	$C_{11}H_{22}O_2$	0.0492	0.216	0.00275	0.0838	0.0573	0.127	+	0.0651	0.0339	0.0760	0.0751	0.116	0.0633	---	0.0770	0.286
Dodecanoic acid[a]	$C_{12}H_{24}O_2$	0.311	0.305	+	+	0.142	0.473	+	+	0.586	0.458	0.151	+	0.144	0.192	+	+
Tridecanoic acid[a]	$C_{13}H_{26}O_2$	0.00664	0.0216	0.0103	0.0496	0.0739	0.0194	0.0799	0.0414	0.0512	0.0146	---	0.0193	0.00812	---	0.104	0.0262
Tetradecanoic acid[a]	$C_{14}H_{28}O_2$	0.0834	0.161	+	0.279	0.327	0.347	0.361	0.146	0.752	0.385	0.655	0.272	0.216	0.116	0.00362	0.431
Pentadecanoic acid[a]	$C_{15}H_{30}O_2$	0.0855	0.117	0.0765	0.0170	0.554	0.349	0.219	0.0462	0.346	0.177	0.264	0.0722	0.118	0.0362	0.00506	0.101
Hexadecanoic acid[a]	$C_{16}H_{32}O_2$	+	0.910	0.605	0.991	4.07	4.23	1.97	1.25	12.8	4.00	9.46	2.30	1.14	0.772	+	5.79
Heptadecanoic acid[a]	$C_{17}H_{34}O_2$	0.0386	0.0808	0.0953	0.105	0.372	0.216	0.130	0.112	0.786	0.139	0.472	0.173	0.0717	0.0289	---	0.279
Octadecanoic acid[a]	$C_{18}H_{36}O_2$	0.662	1.30	+	0.580	2.08	3.89	0.700	0.202	2.91	0.831	0.395	0.145	0.556	0.242	+	1.24
Nonadecanoic acid[a]	$C_{19}H_{38}O_2$	0.00932	0.0279	+	0.0346	0.177	0.129	0.0990	0.0135	0.115	0.0864	0.0755	+	0.0447	0.0137	0.00764	+
Eicosanoic acid[a]	$C_{20}H_{40}O_2$	0.0528	0.228	0.202	0.217	0.849	0.739	0.672	0.341	0.388	0.172	0.262	0.115	0.388	0.0897	0.0293	1.37
Docosanoic acid[a]	$C_{22}H_{44}O_2$	0.276	0.618	+	0.855	6.98	4.04	0.591	5.22	1.37	0.744	1.83	0.480	1.08	0.322	0.132	2.38
Tetracosanoic acid[a]	$C_{24}H_{48}O_2$	0.417	0.671	0.241	0.746	6.58	6.76	4.11	4.71	2.47	1.60	4.30	1.12	1.20	0.716	0.215	1.90
Total *n*-Alkanoic Acids identified		**2.06**	**4.74**	**1.23**	**3.99**	**22.4**	**21.5**	**9.03**	**12.18**	**22.7**	**8.82**	**18.1**	**4.88**	**5.10**	**2.56**	**0.584**	**13.9**
$C_{max.}$		**C_{18}**	**C_{18}**	**C_{16}**	**C_{16}**	**C_{22}**	**C_{24}**	**C_{24}**	**C_{22}**	**C_{16}**	**C_{16}**	**C_{16}**	**C_{16}**	**C_{24}**	**C_{16}**	**C_{24}**	**C_{16}**

***n*-di-Acids**																	
Propanedioic acid[a]	$C_3H_4O_4$	---	---	---	---	0.0076	---	---	---	---	---	0.00631	---	---	---	0.00338	---
Butanedioic acid[a]	$C_4H_6O_4$	0.277	0.927	+	0.556	3.78	1.67	3.06	1.639	0.997	2.32	9.96	2.87	1.30	0.369	2.96	6.50
Pentanedioic acid[a]	$C_5H_8O_4$	0.0821	0.340	+	0.158	1.09	0.382	0.640	0.418	0.390	0.441	1.90	0.509	0.587	0.214	0.859	1.82
Hexanedioic acid[a]	$C_6H_{10}O_4$	0.103	0.157	+	+	0.299	0.123	0.122	0.128	0.172	0.114	0.446	0.152	0.132	0.269	0.114	0.372
Heptanedioic acid[a]	$C_7H_{12}O_4$	0.644	1.57	0.439	1.35	1.94	2.18	4.35	0.473	3.20	3.56	10.2	0.525	2.16	1.63	1.98	1.02
Octanedioic acid[a]	$C_8H_{14}O_4$	1.78	1.50	0.685	1.59	---	0.987	1.14	0.762	0.710	2.13	1.40	0.733	1.34	---	1.12	3.17
Nonanedioic acid[a]	$C_9H_{16}O_4$	0.0491	0.0883	---	0.0702	0.236	0.144	0.131	0.0827	0.173	0.0737	0.164	0.139	0.0603	0.128	0.0515	0.175
Decanedioic acid[a]	$C_{10}H_{18}O_4$	0.0214	0.0688	0.0180	0.0537	0.0516	0.0440	0.101	0.0208	0.102	0.0359	0.109	0.0456	0.0159	0.00657	0.0423	0.0984
Hexadecanedioic acid[a]	$C_{16}H_{30}O_4$	0.0171	---	---	0.0168	0.926	0.445	0.0599	0.457	0.0625	0.0489	0.214	0.105	0.0567	0.0233	0.0166	0.0304
Total di-Acids identified		**2.97**	**4.65**	**1.14**	**3.79**	**8.33**	**5.97**	**9.60**	**3.98**	**5.81**	**8.73**	**24.4**	**5.08**	**5.67**	**2.64**	**7.14**	**13.2**
$C_{max.}$		**C_8**	**C_7**	**C_8**	**C_8**	**C_4**	**C_7**	**C_7**	**C_4**	**C_7**	**C_7**	**C_7**	**C_4**	**C_7**	**C_7**	**C_4**	**C_4**
Resin acids																	
Dehydroabietic acid[a]	$C_{20}H_{28}O_2$	83.1	154	68.0	306	1.18	21.2	6.23	---	0.779	12.3	---	0.659	2.74	1.62	1.30	26.6
Isopimaric acid[a]	$C_{20}H_{30}O_2$	4.71	30.9	10.3	37.7	0.466	3.41	1.03	0.631	---	1.94	0.305	0.0472	---	0.524	0.748	1.80
Pimaric acid[a]	$C_{20}H_{30}O_2$	94.8	198	80.0	355	2.75	27.0	8.51	0.631	0.779	15.1	0.305	0.706	2.74	2.14	2.05	28.5
Abietic acid[a]	$C_{20}H_{30}O_2$	+	12.0	9.07	29.4	0.0661	7.81	---	0.515	+	0.264	---	---	0.00778	0.460	---	---
Total resin acids		**182.6**	**395**	**167**	**728**	**4.46**	**59.4**	**15.8**	**1.78**	**1.56**	**29.7**	**0.609**	**1.41**	**5.50**	**4.74**	**4.09**	**56.9**
Unsaturated acids																	
Linoleic acid ($C_{18:2}$)[a]	$C_{18}H_{32}O_2$	0.5098	1.9445	0.8519	1.6762	2.7905	2.7324	1.6494	1.6611	1.7984	0.8594	3.4967	0.8644	1.0086	0.8726	0.3794	2.7991
Other Acids[b]		**20.8**	**56.5**	**21.2**	**87.4**	**81.7**	**109**	**64.6**	**58.4**	**52.8**	**80.1**	**83.9**	**47.5**	**71.2**	**16.6**	**45.0**	**172.8**
Alkyl ester acids[b]		**0.182**	**1.10**	**0.688**	**1.40**	**0.423**	**0.687**	**0.411**	**1.19**	**0.817**	**0.444**	**0.198**	**0.416**	**0.136**	**0.183**	**0.0210**	**0.656**

Anhydrosugars																	
Galactosan[a]	$C_6H_{10}O_5$	114	81.8	37.6	170	56.0	48.6	41.4	35.2	34.9	40.8	38.7	66.0	94.6	23.3	98.1	177
Mannosan[a]	$C_6H_{10}O_5$	232	237	108	+	42.3	115	91.5	15.9	12.5	81.2	15.2	26.9	66.6	289	45.9	61.3
Levoglucosan[a]	$C_6H_{10}O_5$	335	291	148	378	374	159	301	101	205	126	106	186	463	+	506	582
Total Anhydrosugars		**681**	**610**	**294**	**548**	**473**	**322**	**434**	**152**	**253**	**248**	**160**	**279**	**624**	**312**	**650**	**820**
Other sugars[b]		**35.0**	**140**	**83.4**	**345**	**206**	**147**	**293**	**113**	**70.4**	**150**	**51.0**	**82.4**	**170**	**83.6**	**274**	**402**
Other Compounds[b]		**14.0**	**36.4**	**13.8**	**72.7**	**15.7**	**46.6**	**18.9**	**9.87**	**73.1**	**89.2**	**19.0**	**25.9**	**133**	**33.4**	**57.5**	**68.7**

Table A2 (continued)

Compounds	**Formula**	**Olive**				**Cork oak**				**Portuguese oak**				**Briquettes**			
		W_Hot	**W_Cold**	**F_Hot**	**F_Cold**	**W_Hot**	**W_Cold**	**F_Hot**	**F_Cold**	**W_Hot**	**W_Cold**	**F_Hot**	**F_Cold**	**W_Hot**	**W_Cold**	**F_Hot**	**F_Cold**
***n*-Alkanes**																	
Tetradecane[a]	$C_{14}H_{30}$	0.0601	---	0.00518	0.00304	0.00970	0.251	---	0.0027	0.00460	0.0453	0.100	0.0317	0.222	0.0413	---	0.0459
Pentadecane[a]	$C_{15}H_{32}$	---	---	---	---	---	---	---	---	---	0.0526	---	---	---	---	---	---
Hexadecane[a]	$C_{16}H_{34}$	0.0225	---	0.00387	0.0103	0.0120	0.110	---	---	0.00536	0.0577	0.0446	0.0206	0.0965	0.145	---	---
Heptadecane[a]	$C_{17}H_{36}$	+	+	0.00203	0.00108	+	0.0406	+	+	+	0.0147	0.0111	0.000840	+	0.0667	0.000236	0.00423
Octadecane[a]	$C_{18}H_{38}$	0.00473	+	+	0.00928	+	0.0142	+	+	+	0.0164	0.0280	0.000307	0.0835	0.0375	0.00474	0.00740
Pristane[a]	$C_{19}H_{40}$	---	---	---	---	---	---	---	---	---	---	---	---	0.0207	---	0.00124	---
Nonadecane[a]	$C_{19}H_{40}$	0.00940	0.00515	---	0.00447	0.0113	0.0276	---	---	0.00279	0.0116	---	0.00684	0.0679	0.0521	0.0124	0.0199
Eicosane[a]	$C_{20}H_{42}$	0.0123	+	0.0136	0.00483	+	0.0210	+	+	+	0.00555	0.0158	0.00948	0.0652	0.0869	0.0202	0.0381
Heneicosane[a]	$C_{21}H_{44}$	0.0450	+	0.0544	0.0244	+	0.0316	+	+	+	+	0.0188	0.00399	0.0695	0.113	0.0402	0.0484
Docosane[a]	$C_{22}H_{46}$	0.00343	+	+	0.00356	+	0.00558	+	+	+	+	0.0193	+	+	0.148	0.0465	0.0562
Tricosane[a]	$C_{23}H_{48}$	+	+	0.109	0.0944	+	+	0.0165	0.00469	+	+	0.105	0.0112	+	0.130	0.105	0.171
Tetracosane[a]	$C_{24}H_{50}$	+	+	+	+	+	+	+	+	+	+	+	+	+	0.0938	+	+

Pentacosane[a]	$C_{25}H_{52}$	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Hexacosane[a]	$C_{26}H_{54}$	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Heptacosane[a]	$C_{27}H_{56}$	+	+	+	+	+	+	+	+	+	+	0.0532	+	+	+	+	0.0287
Octacosane[a]	$C_{28}H_{58}$	+	+	+	+	+	+	+	+	+	+	0.0668	+	+	+	+	0.126
Nonacosane[a]	$C_{29}H_{60}$	+	+	+	+	+	+	+	+	+	+	0.100	+	+	+	+	0.142
Triacontane[a]	$C_{30}H_{62}$	+	+	+	+	+	+	+	+	+	+	0.119	+	+	+	+	0.204
Hentriacontane[a]	$C_{31}H_{64}$	+	+	+	0.0220	+	+	+	+	+	+	0.158	+	+	+	0.0235	0.202
Dotriacontane[a]	$C_{32}H_{66}$	+	+	+	0.00980	+	+	+	+	+	+	0.0465	+	+	0.0218	0.00448	0.101
Tritriacontane[a]	$C_{33}H_{68}$	+	+	+	+	+	0.00299	+	+	+	+	0.0300	+	+	0.0617	+	0.0656
Tetratriacontane[a]	$C_{34}H_{70}$	+	+	---	---	+	+	---	---	+	+	0.0224	0.0190	+	+	0.00706	0.0455
Total *n*-Alkanes identified		**0.157**	**0.00515**	**0.188**	**0.187**	**0.0330**	**0.504**	**0.0165**	**0.00742**	**0.0128**	**0.204**	**0.938**	**0.104**	**0.626**	**1.00**	**0.266**	**1.31**
$C_{max.}$		**C_{14}**	**C_{19}**	**C_{23}**	**C_{23}**	**C_{16}**	**C_{14}**	**C_{23}**	**C_{23}**	**C_{16}**	**C_{16}**	**C_{31}**	**C_{14}**	**C_{14}**	**C_{22}**	**C_{23}**	**C_{30}**
Total other Alkanes[b]		**2.47**	**3.04**	**2.16**	**1.75**	**2.00**	**2.20**	**0.966**	**1.15**	**1.18**	**1.30**	**0.870**	**1.26**	**3.32**	**3.76**	**2.09**	**0.87**
Σ Alkanes		**2.63**	**3.05**	**2.35**	**1.94**	**2.03**	**2.70**	**0.982**	**1.15**	**1.19**	**1.50**	**1.81**	**1.37**	**3.95**	**4.76**	**2.36**	**2.18**
***n*-Alkenes**																	
Hexadecene[a]	$C_{16}H_{32}$	0.0535	---	0.00687	---	0.00909	---	---	---	0.00312	---	0.0817	---	0.180	---	---	0.0494
Octadecene[a]	$C_{18}H_{36}$	0.0198	+	0.00382	0.00344	+	+	+	+	+	+	0.0447	0.0136	0.0606	+	0.00350	0.0312
Nonadecene[a]	$C_{19}H_{38}$	0.0280	---	---	---	---	0.0233	---	---	---	---	---	0.0187	---	---	---	0.0461
Eicosene[a]	$C_{20}H_{40}$	0.0864	0.0158	0.0366	0.0275	0.0135	0.0472	+	0.00578	0.0318	0.0288	0.0504	0.158	0.104	0.0967	0.0265	0.0691
Heneicosene[a]	$C_{21}H_{42}$	0.0970	0.0195	0.0914	0.0298	0.00967	0.0616	0.00379	0.00528	0.0182	0.0198	0.0305	0.0411	0.0720	0.0909	0.0317	0.0433
Docosene[a]	$C_{22}H_{44}$	0.175	0.0262	0.0909	0.0478	0.0145	0.111	0.0208	0.0137	0.0410	0.0277	0.123	0.0991	0.132	0.111	0.0537	0.0761
cis-9-Tricosene[a]	$C_{23}H_{46}$	0.101	0.0198	+	+	0.0138	0.0712	+	+	0.0213	0.0232	+	+	0.0693	0.0829	+	+
Tetracosene[a]	$C_{24}H_{48}$	0.111	0.0295	0.0595	0.0507	---	0.0455	0.00717	0.00308	0.0237	0.0147	0.0461	0.0316	0.0566	0.0889	0.0304	0.0518
Pentacosene[a]	$C_{25}H_{50}$	0.0387	0.0120	0.0228	0.0167	---	---	---	0.00615	---	---	0.00237	0.0123	---	---	---	---
Hexacosene[a]	$C_{26}H_{52}$	0.0954	0.0413	0.0561	0.0406	---	---	---	---	---	---	---	---	0.879	---	---	---
Octacosene[a]	$C_{28}H_{54}$	0.0766	0.0225	0.0351	---	---	---	---	---	---	---	---	---	---	---	---	---
Total *n*-Alkenes identified		**0.882**	**0.187**	**0.403**	**0.217**	**0.0606**	**0.360**	**0.0317**	**0.0340**	**0.139**	**0.114**	**0.378**	**0.374**	**1.55**	**0.470**	**0.146**	**0.367**

$C_{max.}$		**C_{22}**	**C_{26}**	**C_{21}**	**C_{24}**	**C_{22}**	**C_{22}**	**C_{22}**	**C_{22}**	**C_{22}**	**C_{20}**	**C_{22}**	**C_{20}**	**C_{26}**	**C_{22}**	**C_{22}**	**C_{22}**
Total other Alkenes[b]		**0.601**	**0.742**	**0.464**	**0.217**	**0.432**	**0.537**	**0.230**	**0.292**	**0.241**	**0.231**	**0.121**	**0.363**	**0.186**	**0.152**	**0.346**	**0.198**
Σ Alkenes		**1.48**	**0.928**	**0.867**	**0.434**	**0.492**	**0.896**	**0.261**	**0.326**	**0.380**	**0.346**	**0.499**	**0.737**	**1.74**	**0.623**	**0.492**	**0.565**
PAHs																	
Naphthalene[a]	$C_{10}H_8$	0.00970	0.0121	0.00368	0.000155	+	0.0172	0.000102	0.00230	+	0.000636	---	---	0.0238	0.00730	0.00326	0.00267
Acenaphthylene[a]	$C_{12}H_8$	0.00248	0.00119	0.000345	0.000932	---	0.00214	0.00114	0.0368	---	0.000122	---	0.00346	0.000781	0.000637	0.000684	0.00153
Acenaphthene[a]	$C_{12}H_{10}$	---	---	---	---	0.000382	---	---	---	0.000262	---	---	---	---	---	---	---
Fluorene[a]	$C_{13}H_{10}$	0.00623	0.00755	0.00148	0.00574	---	0.00720	0.00347	0.0485	---	0.00153	---	0.0120	---	0.00356	0.00166	0.00454
Phenanthrene[a]	$C_{14}H_{10}$	0.167	0.260	0.0438	0.164	0.00166	0.117	0.0610	0.221	0.000893	0.0534	0.114	0.227	0.0291	0.123	0.0260	0.108
Anthracene[a]	$C_{14}H_{10}$	0.0591	0.101	0.0184	0.0677	0.111	0.0453	0.0220	0.0986	0.0579	0.0188	0.0352	0.101	0.0115	0.0403	0.00985	0.0391
Fluoranthene[a]	$C_{16}H_{10}$	0.361	0.314	0.0535	0.273	0.0424	0.0740	0.107	0.148	0.0236	0.0481	0.488	0.243	0.196	0.102	0.0282	0.122
Pyrene[a]	$C_{16}H_{10}$	0.450	0.435	0.0632	0.488	0.195	0.0915	0.113	0.230	0.0958	0.0812	0.670	0.459	0.219	0.119	0.0352	0.136
p-terphenyl[a]	$C_{18}H_{14}$	0.00494	0.0218	0.000772	0.00300	0.244	0.00335	0.00117	0.00365	0.136	0.000482	0.0264	0.00284	0.00189	0.00114	0.000269	0.00105
Retene[a]	$C_{18}H_{18}$	0.0512	0.205	+	0.235	+	0.125	+	0.00653	0.000871	0.0905	+	0.00936	0.362	0.652	0.0575	0.235
Benzo[a]anthracene[a]	$C_{18}H_{12}$	0.122	0.148	0.0215	0.140	---	0.0220	0.0358	0.0544	0.00251	0.0200	0.229	0.116	0.154	0.0284	0.00737	0.0302
Chrysene[a]	$C_{18}H_{12}$	0.130	0.108	0.0199	0.108	0.0737	0.0228	0.0357	0.0508	0.0321	0.0178	0.101	0.0997	0.219	0.0312	0.00854	0.0361
Benzo[b]fluoranthene[a]	$C_{20}H_{12}$	0.0372	0.0778	0.0127	0.0523	0.0733	0.00850	0.0115	0.0216	0.0378	0.00655	0.0644	0.0535	0.116	0.0121	0.00198	0.00950
Benzo[k]fluoranthene[a]	$C_{20}H_{12}$	0.0290	0.0484	0.00802	0.0390	0.0153	0.00533	0.00801	0.0135	0.00882	0.00763	0.0366	0.0316	0.0850	0.00672	0.00208	0.00771
Benzo[j]fluoranthene[a]	$C_{20}H_{12}$	0.0433	0.0645	0.0111	0.0482	---	0.00831	0.0132	0.0171	---	0.00901	0.0530	0.0426	0.119	0.0112	0.00197	0.00815
Benzo[a]pyrene[a]	$C_{20}H_{12}$	0.0641	0.0913	0.0127	0.0943	0.0161	0.0104	0.0227	0.0344	0.00841	0.0112	0.130	0.0884	0.0887	0.0127	0.00248	0.0131
Benzo[e]pyrene[a]	$C_{20}H_{12}$	0.0569	0.0566	0.0107	0.0573	0.0218	0.00983	0.0171	0.0268	0.00925	0.00684	0.0925	0.0605	0.139	0.0118	0.00230	0.0124
Perylene[a]	$C_{20}H_{12}$	0.0108	0.0148	0.00183	0.0127	0.0445	0.00241	0.00336	0.00530	0.0165	0.00258	---	0.0137	0.0146	0.00318	0.000430	0.00215
Indeno[1,2,3-cd]pyrene[a]	$C_{22}H_{12}$	0.0383	0.0527	0.00712	0.0522	0.00639	0.00425	0.0124	0.0173	0.00241	0.00627	0.0516	0.0481	0.0511	0.00656	---	0.00575
Dibenzo[a,h]anthracene[a]	$C_{24}H_{14}$	0.00503	0.00608	0.00123	0.00630	0.0171	0.000633	0.00163	0.00242	0.00739	0.00102	0.0271	0.00551	0.00743	0.00110	---	---
Benzo[ghi]perylene[a]	$C_{22}H_{12}$	0.0286	0.0402	0.00476	0.0370	0.00232	0.00355	0.00910	0.0128	0.00110	0.00461	0.0361	0.0407	0.0386	0.00502	---	0.00323
Total PAHs identified		**1.68**	**2.07**	**0.297**	**1.88**	**0.865**	**0.581**	**0.480**	**1.05**	**0.442**	**0.388**	**2.15**	**1.66**	**1.88**	**1.18**	**0.190**	**0.778**

Total other PAHs[b]		**7.94**	**4.75**	**4.52**	**7.29**	**2.41**	**2.54**	**3.89**	**3.86**	**1.83**	**6.14**	**3.65**	**2.39**	**8.16**	**14.5**	**5.92**	**6.75**
Σ PAHs		**9.61**	**6.82**	**4.81**	**9.18**	**3.28**	**3.12**	**4.37**	**4.91**	**2.27**	**6.53**	**5.81**	**4.05**	**10.0**	**15.7**	**6.11**	**7.52**
Oxygenated aromatics																	
9-Fluorenone[a]	$C_{13}H_8O$	0.134	0.0401	0.171	0.0203	0.0427	0.0868	0.0393	0.124	0.0299	0.00418	0.0484	0.0959	---	0.170	0.00576	0.0283
9,10-Anthracenedione[a]	$C_{14}H_8O_2$	0.0657	0.0283	0.113	0.0129	0.0306	---	0.0234	0.0365	0.0184	---	0.0266	0.0383	0.271	0.553	0.0275	0.164
2,6-di-tert-butyl-1,4-benzoquinone[a]	$C_{14}H_{20}O_2$	0.0902	0.0152	0.0131	0.0461	0.106	0.0331	0.0180	0.000789	0.00177	0.0129	0.0431	0.0169	0.0503	0.0231	0.0136	0.0165
Aldehydes[b]		**0.0927**	**0.221**	**0.0415**	**0.0761**	**0.145**	**0.236**	**0.0894**	**0.110**	**0.0648**	**0.0942**	**0.118**	**0.0616**	**0.0596**	**0.306**	**0.136**	**0.119**
Ketones																	
2-Tridecanone[a]	$C_{13}H_{26}O$	0.0405	0.0330	0.0320	0.0387	0.0357	0.581	0.0284	0.0257	0.0130	0.133	0.0524	0.0303	0.0124	0.0414	0.0371	0.0150
2-Pentadecanone[a]	$C_{15}H_{30}O$	0.115	0.227	0.101	0.148	0.147	0.488	0.129	0.117	0.0513	0.310	0.192	0.0989	0.114	0.319	0.145	0.207
3-Hexadecanone[a]	$C_{16}H_{32}O$	0.00105	0.00111	---	0.000381	0.000968	0.00176	0.000541	0.00246	0.000402	0.000759	0.000501	0.00100	0.00120	0.00161	0.000631	0.00115
2-Octadecanone[a]	$C_{18}H_{36}O$	0.0233	---	0.0173	0.00459	0.00818	0.0207	0.00451	---	0.00634	---	0.00791	0.0121	0.0226	0.0129	---	0.0103
Total Ketones identified		**0.180**	**0.261**	**0.151**	**0.191**	**0.192**	**1.09**	**0.162**	**0.145**	**0.0711**	**0.444**	**0.253**	**0.142**	**0.150**	**0.375**	**0.182**	**0.233**
Other Ketones[b]		**0.0606**	**0.297**	---	**0.0646**	**0.0992**	**0.411**	**0.140**	**0.209**	**0.119**	**0.154**	**0.522**	**0.207**	**0.497**	**0.190**	**0.218**	**0.250**
Σ Ketones		**0.240**	**0.558**	**0.151**	**0.256**	**0.292**	**1.50**	**0.302**	**0.354**	**0.190**	**0.598**	**0.776**	**0.349**	**0.648**	**0.565**	**0.400**	**0.483**
Triterpenoids																	
4-Cholesten-3-one[a]	$C_{27}H_{44}O$	---	---	0.000785	---	---	0.0603	---	---	---	---	---	0.0000423	---	---	---	0.00312
Urs-12-en-one[a]	$C_{30}H_{48}O$	0.00155	---	0.0144	---	0.000852	0.0566	0.000715	0.00238	0.00183	---	0.00531	0.00680	0.00188	0.0170	0.000503	0.00146
Lupeol[a]	$C_{30}H_{50}O$	---	0.134	0.0676	0.0779	0.208	0.427	0.0508	0.0821	0.181	0.0557	0.0917	0.0552	0.0486	0.191	0.110	0.186

Terpenoids																	
(-)-Isopulegol[a]	$C_{10}H_{18}O$	0.00609	0.0400	0.0135	0.0225	0.0418	0.0260	0.0310	---	0.0151	0.0152	0.0410	0.0291	0.00583	0.00957	0.0254	---
(1S,2S,3R,5S) -(+)-2,3-Pinanedio[a]	$C_{10}H_{18}O_2$	2.24	2.39	1.26	2.17	4.31	3.76	3.60	0.896	11.5	11.3	5.91	7.99	0.344	3.02	3.08	3.13
Phenolic compounds																	
4-Octylphenol[a]	$C_{14}H_{22}O$	0.344	0.258	0.0759	0.0741	0.448	0.595	0.0998	0.202	0.236	0.234	0.0476	0.168	---	0.243	0.0299	0.384
Vanillic acid[a]	$C_8H_8O_4$	2.66	+	0.811	1.41	1.34	7.44	1.59	0.694	2.66	3.84	1.53	3.05	9.52	17.7	8.84	10.1
Syringic acid[a]	$C_9H_{10}O_5$	5.30	+	2.06	2.16	4.93	14.2	5.41	2.42	10.6	12.5	8.16	8.46	20.9	34.8	12.9	8.54
Sinapic acid[a]	$C_{11}H_{12}O_5$	0.0606	+	0.0464	0.0519	0.100	0.128	0.108	0.0451	0.126	0.0685	0.0994	0.0760	0.0390	0.140	0.113	0.116
Coniferyl alcohol[a]	$C_{10}H_{12}O_3$	1.52	3.14	0.829	4.85	0.756	1.49	2.03	4.11	0.511	0.188	0.681	2.94	0.00214	1.33	0.268	0.673
Sinapyl alcohol[a]	$C_{11}H_{14}O_4$	0.152	0.252	0.0362	0.317	0.0476	0.0483	0.229	1.76	0.153	0.0208	0.0724	0.938	0.000450	0.0265	0.0160	0.0267
Catechol[a]	$C_6H_6O_2$	4.63	+	6.21	11.6	34.0	24.1	29.2	8.97	35.2	48.2	36.9	14.7	15.6	38.7	32.0	38.2
Resorcinol[a]	$C_6H_6O_2$	---	+	0.811	1.32	1.90	---	2.16	1.48	2.19	1.18	2.18	2.32	---	1.10	16.2	---
Methylcatechol[a]	$C_7H_8O_2$	2.98	---	6.33	9.57	37.3	13.1	20.8	8.71	34.0	34.2	24.2	13.6	6.05	51.9	23.4	18.5
Pyrogallol[a]	$C_6H_6O_3$	---	+	12.3	29.0	59.7	29.0	37.7	29.5	50.9	110	53.1	28.3	---	77.5	40.7	36.6
Vanillin[a]	C_8H_8O	8.38	6.89	17.3	5.67	7.09	7.56	8.18	24.7	7.02	6.53	11.2	14.0	---	13.0	16.2	6.65
(±)-α-Tocopherol=Vitamin E[a]	$C_{29}H_{50}O_2$	0.0512	0.0454	0.0251	0.0610	0.217	0.249	0.221	0.234	0.302	0.260	0.223	0.260	0.00196	0.0154	0.0116	0.0189
Other Phenols[b]		8.89	0.0956	4.81	2.71	5.51	0.256	2.29	2.23	1.87	0.259	6.41	3.59	9.50	0.225	2.50	6.07
Total phenolic compounds		**35.0**	**10.7**	**51.6**	**68.8**	**153**	**98.1**	**110**	**85.0**	**146**	**218**	**145**	**92.4**	**61.6**	**237**	**153**	**126**
n-Alcohols																	
n-Decanol[a]	$C_{10}H_{22}O$	0.00268	0.00284	0.00106	0.00341	0.00422	0.00514	0.00394	0.0263	0.00247	0.00240	0.00294	0.00408	0.00382	0.000841	0.00174	0.00210
n-Pentadecanol[a]	$C_{15}H_{32}O$	0.00175	0.000412	0.00321	0.00786	0.00182	0.00220	0.00721	0.0243	0.000814	0.00614	0.00810	0.0247	0.00258	0.000531	0.0111	0.00846
n-Octadecanol[a]	$C_{18}H_{38}O$	+	+	0.0233	0.0164	+	+	0.0522	0.0589	0.375	+	0.229	0.891	0.368	+	0.0919	0.0646
n-Docosanol[a]	$C_{20}H_{42}O$	0.106	0.112	0.0836	0.108	0.0547	0.676	0.162	1.26	0.283	0.0392	1.51	0.580	0.178	0.237	0.171	0.204
n-Tricosanol[a]	$C_{23}H_{48}O$	0.0942	0.122	0.917	0.157	0.0109	0.0446	0.0106	0.203	0.0457	0.00608	0.920	0.183	0.0208	0.0271	0.0163	0.0229
n-Pentacosanol[a]	$C_{25}H_{52}O$	0.102	0.120	0.781	0.158	0.0104	0.0149	0.0148	0.401	0.104	0.0150	1.10	0.415	0.00801	0.0495	0.0287	0.0350

n-Heptacosanol[a]	$C_{27}H_{56}O$	0.0156	0.0524	0.0247	0.0267	0.0221	0.0178	---	---	0.00642	0.00303	0.180	---	---	0.0211	---	---
n-Octacosanol[a]	$C_{28}H_{58}O$	1.04	0.829	0.571	0.313	0.00446	0.0158	0.00367	0.00617	0.00428	0.00507	2.36	0.0215	0.0326	0.0541	0.0455	0.0487
n-Tricontanol[a]	$C_{30}H_{62}O$	0.545	0.383	0.226	0.132	0.00732	0.0152	+	+	0.00543	0.00653	2.53	0.0358	0.00522	0.0108	0.0127	0.0117
Total *n*-Alkanols identified		**1.91**	**1.62**	**2.63**	**0.922**	**0.116**	**0.792**	**0.254**	**1.98**	**0.827**	**0.0835**	**8.84**	**2.16**	**0.619**	**0.401**	**0.379**	**0.398**
$C_{max.}$		**C_{28}**	**C_{28}**	**C_{23}**	**C_{28}**	**C_{22}**	**C_{22}**	**C_{22}**	**C_{22}**	**C_{18}**	**C_{22}**	**C_{30}**	**C_{18}**	**C_{18}**	**C_{22}**	**C_{22}**	**C_{22}**
Other Alcohols[b]		**36.7**	**0.0324**	**37.6**	**72.0**	**3.94**	**2.14**	**3.24**	**2.66**	**0.472**	**17.0**	**5.67**	**1.99**	**0.734**	**0.736**	**20.0**	**6.58**
Σ Alcohols		**38.6**	**1.65**	**40.2**	**72.9**	**4.06**	**2.93**	**3.49**	**4.64**	**1.30**	**17.1**	**14.5**	**4.15**	**1.35**	**1.14**	**20.4**	**6.98**
Phytosterols and derivatives																	
Stigmasterol[a]	$C_{29}H_{48}O$	0.244	0.396	0.118	0.205	0.0537	0.0555	0.0257	0.0358	0.110	0.0410	0.0619	0.0888	0.0356	0.583	0.162	0.211
β-Sitosterol[a]	$C_{29}H_{50}O$	4.64	5.03	4.60	3.62	4.27	4.02	3.30	5.71	2.15	1.75	2.37	5.26	0.760	4.34	2.23	3.20
Other Phytosterols and derivatives[b]		**1.25**	**2.17**	**0.514**	**1.03**	**1.14**	**3.27**	**0.699**	**0.851**	**0.617**	**1.21**	**1.08**	**1.03**	**1.53**	**1.37**	**1.26**	**0.932**
***n*-Alkanoic Acids**																	
Octanoic acid[a]	$C_8H_{16}O_2$	0.0107	---	0.000358	0.0155	0.0182	0.0305	0.0221	0.0118	0.0358	0.0139	0.0275	0.0497	0.0327	0.0235	0.0124	0.0146
Nonanoic acid[a]	$C_9H_{18}O_2$	0.0145	---	+	0.0123	0.0227	0.0380	0.0117	0.00575	0.0444	0.0272	0.0226	0.0501	0.0471	0.0352	0.00553	0.00542
Decanoic acid[a]	$C_{10}H_{20}O_2$	0.0185	---	0.00196	0.0204	0.0249	0.0453	0.0204	0.0111	0.0625	0.0694	+	0.0417	0.0517	0.0380	0.0198	0.0366
Undecanoic acid[a]	$C_{11}H_{22}O_2$	0.0497	---	0.0309	0.0345	0.0477	0.0409	0.0404	0.0234	0.0830	0.170	0.0889	0.0447	0.0918	0.0988	0.125	0.109
Dodecanoic acid[a]	$C_{12}H_{24}O_2$	0.0904	---	+	+	0.234	0.405	+	+	0.406	0.752	+	0.0142	0.173	0.479	0.135	+
Tridecanoic acid[a]	$C_{13}H_{26}O_2$	0.0968	---	0.198	---	0.0148	0.0231	0.0321	---	---	---	0.00874	0.0107	---	0.0297	0.00888	0.0210
Tetradecanoic acid[a]	$C_{14}H_{28}O_2$	0.304	---	+	0.0882	0.185	0.433	0.253	0.0393	0.395	0.193	0.277	0.131	0.484	0.239	0.133	0.161
Pentadecanoic acid[a]	$C_{15}H_{30}O_2$	0.222	---	+	0.0724	0.106	0.157	0.131	0.0275	0.220	0.0348	0.00906	0.0908	0.232	0.0596	0.0955	0.132
Hexadecanoic acid[a]	$C_{16}H_{32}O_2$	6.17	---	+	1.520	1.45	3.69	2.25	0.0856	3.00	2.25	5.03	0.896	2.05	11.1	4.02	3.31
Heptadecanoic acid[a]	$C_{17}H_{34}O_2$	0.348	---	---	0.106	0.102	0.151	0.123	0.0160	0.163	0.0620	0.0750	0.0688	0.136	0.252	0.150	0.150
Octadecanoic acid[a]	$C_{18}H_{36}O_2$	1.10	---	+	0.124	0.557	0.875	0.191	+	0.818	0.485	2.87	0.0665	2.22	1.92	0.692	0.349

Nonadecanoic acid[a]	$C_{19}H_{38}O_2$	0.110	---	0.00702	0.0369	0.0430	0.0957	0.0276	0.0147	0.066	---	0.0522	0.0397	0.0886	0.0911	0.0495	0.0495
Eicosanoic acid[a]	$C_{20}H_{40}O_2$	0.562	---	0.0278	0.214	0.0802	0.320	0.0897	0.0142	0.381	0.357	3.54	0.159	0.302	0.302	0.178	0.152
Docosanoic acid[a]	$C_{22}H_{44}O_2$	2.00	---	0.144	0.786	0.262	0.939	0.421	0.101	1.098	0.518	15.2	0.604	1.329	1.21	0.590	0.507
Tetracosanoic acid[a]	$C_{24}H_{48}O_2$	2.07	---	0.172	0.557	0.314	1.42	0.560	0.198	2.234	1.32	12.6	1.25	1.699	1.92	0.837	0.695
Total *n*-Alkanoic Acids identified		**13.2**		**0.582**	**3.59**	**3.46**	**8.66**	**4.17**	**0.548**	**9.00**	**6.26**	**39.9**	**3.52**	**8.94**	**17.8**	**7.05**	**5.69**
$C_{max.}$		**C_{16}**		**C_{13}**	**C_{16}**	**C_{16}**	**C_{16}**	**C_{16}**	**C_{24}**	**C_{16}**	**C_{16}**	**C_{22}**	**C_{24}**	**C_{18}**	**C_{16}**	**C_{16}**	**C_{16}**
***n*-di-Acids**																	
Propanedioic acid[a]	$C_3H_4O_4$	---	---	0.00125	---	---	---	0.00242	---	---	---	0.000651	0.00205	---	---	0.00475	---
Butanedioic acid[a]	$C_4H_6O_4$	0.972	---	1.84	1.14	1.94	1.90	3.39	1.00	4.43	1.35	3.32	3.73	3.57	0.835	2.50	1.47
Pentanedioic acid[a]	$C_5H_8O_4$	0.287	---	0.344	0.387	0.450	0.313	0.628	0.314	0.841	0.223	0.746	0.716	1.23	0.362	0.847	0.613
Hexanedioic acid[a]	$C_6H_{10}O_4$	1.43	---	0.425	+	0.0944	0.150	0.0718	0.0227	0.108	---	0.401	0.0832	0.286	---	0.154	0.0946
Heptanedioic acid[a]	$C_7H_{12}O_4$	2.26	---	2.97	1.94	3.34	0.280	3.77	2.82	2.61	1.06	0.529	2.71	3.28	2.97	2.72	1.92
Octanedioic acid[a]	$C_8H_{14}O_4$	2.22	---	0.667	0.700	0.948	1.00	0.638	0.275	1.07	1.14	0.978	1.10	2.39	4.54	1.55	2.24
Nonanedioic acid[a]	$C_9H_{16}O_4$	0.208	---	0.376	0.179	0.0586	0.0969	0.0619	0.0394	0.160	0.122	0.0857	0.179	0.338	0.142	0.161	0.164
Decanedioic acid[a]	$C_{10}H_{18}O_4$	0.0302	---	0.0199	0.0101	0.0186	0.0217	0.0227	0.0462	0.0414	0.0175	0.0481	0.0396	0.0700	0.0495	0.0336	0.0411
Hexadecanedioic acid[a]	$C_{16}H_{30}O_4$	0.121	---	0.111	0.275	0.0120	0.0681	0.0270	0.0598	0.115	0.0910	0.0437	0.129	0.0290	0.0866	0.0497	0.0743
Total di-Acids identified		**7.53**		**6.75**	**4.63**	**6.86**	**3.83**	**8.61**	**4.59**	**9.38**	**4.01**	**6.15**	**8.69**	**11.2**	**8.98**	**8.01**	**6.62**
$C_{max.}$		**C_7**		**C_7**	**C_7**	**C_7**	**C_4**	**C_7**	**C_7**	**C_4**	**C_4**	**C_4**	**C_4**	**C_4**	**C_8**	**C_7**	**C_8**
Resin acids																	
Dehydroabietic acid[a]	$C_{20}H_{28}O_2$	0.504	5.43	---	8.14	0.385	15.9	---	1.24	0.256	25.5	50.9	1.13	7.60	21.5	6.53	13.7
Isopimaric acid[a]	$C_{20}H_{30}O_2$	0.165	0.982	0.451	0.860	0.0630	5.61	0.117	---	0.118	2.25	2.80	0.462	2.26	5.88	3.54	3.19
Pimaric acid[a]	$C_{20}H_{30}O_2$	0.669	6.41	0.754	9.00	0.448	26.0	0.471	1.24	0.374	30.8	53.7	1.59	10.6	29.3	10.1	18.5
Abietic acid[a]	$C_{20}H_{30}O_2$	+	3.25	1.13	---	0.0151	11.7	---	0.285	0.00859	1.60	1.47	0.235	0.0390	0.429	---	---
Total resin acids		**1.34**	**16.1**	**2.33**	**18.0**	**0.910**	**59.2**	**0.587**	**2.76**	**0.757**	**60.2**	**109**	**3.42**	**20.5**	**57.1**	**20.1**	**35.3**

Unsaturated acids																
Linoleic acid ($C_{18:2}$)[a]	$C_{18}H_{32}O_2$	5.2711	---	0.1131	2.7698	1.1269	2.4602	1.8456	0.5032	3.9908	2.9244	2.0077	1.6733	1.2094	7.0466	2.9700	3.2234
Other Acids[b]		**55.3**	---	**17.9**	**39.0**	**55.6**	**132**	**44.5**	**31.1**	**93.1**	**134**	**104**	**82.2**	**160**	**177**	**146**	**101**
Alkyl ester acids[b]		**0.617**	**0.771**	**0.364**	**0.376**	**0.217**	**1.01**	**0.144**	**0.330**	**0.119**	**0.233**	**0.818**	**0.284**	**0.278**	**0.773**	**0.248**	**0.429**
Anhydrosugars																	
Galactosan[a]	$C_6H_{10}O_5$	19.4	---	24.4	30.7	53.1	53.0	44.7	25.9	65.2	125	50.3	55.7	226	191	133	183
Mannosan[a]	$C_6H_{10}O_5$	30.1	---	23.5	58.1	52.9	108	26.4	15.2	+	320	91.0	+	31.9	293	85.4	265
Levoglucosan[a]	$C_6H_{10}O_5$	99.2	---	79.6	133	293	241	184	112	349	506	327	199	948	410	+	532
Total Anhydrosugars		**149**	---	**128**	**222**	**399**	**403**	**255**	**153**	**414**	**950**	**469**	**254**	**1206**	**894**	**218**	**979**
Other sugars[b]		**199**	---	**96.8**	**65.7**	**77.4**	**88.5**	**87.5**	**44.3**	**190**	**216**	**166**	**177**	**307**	**284**	**484**	**192**
Other Compounds[b]		**24.1**	---	**27.3**	**65.9**	**97.3**	**105**	**15.2**	**9.86**	**72.9**	**96.0**	**42.8**	**19.1**	**83.0**	**201**	**13.8**	**42.6**

(---) not detected; (+) detected, but not quantified, because of abundances close to the detection limit.

W_Hot - Woodstove with hot start

W_Cold - Woodstove with cold start

F_Hot - Fireplace with hot start

F_Cold - Fireplace with cold start

[a] compound identified with authentic standards

[b] group of compounds identified with surrogate standards

Supplementary Material A3

The concentrations of all organic compounds from Chapter 5.

Table A3 Normalised particulate OC emissions (µg compound g^{-1} OC)

		Potatoes			***Arable weed vegetation***			***Stalks of collard greens, etc***			***Container***		
Compound	**Formula**	$PM_{2.5}$	$PM_{2.5-10}$	$PM_{>10}$	$PM_{2.5}$	$PM_{2.5-10}$	$PM_{>10}$	$PM_{2.5}$	$PM_{2.5-10}$	$PM_{>10}$	$PM_{2.5}$	$PM_{2.5-10}$	$PM_{>10}$
***n*-Alkanes**													
Tridecane	$C_{13}H_{28}$	10.7		0.60	17.8	1.36	0.68		0.89	0.02			0.22
Tetradecane	$C_{14}H_{30}$	11.1		4.58	34.5	4.46	2.45	65.8	3.55	2.73			5.53
Pentadecane	$C_{15}H_{32}$	0.58		15.4	9.53	3.13	2.85	52.8	0.78	9.21	12.8	0.27	24.5
Hexadecane	$C_{16}H_{34}$	350	22.9	4.83	195	5.23	4.35	360	12.3		65.9	121	62.2
Heptadecane	$C_{17}H_{36}$			67.3	311	0.09	24.1	2808		39.5	6.79		55.6
Octadecane	$C_{18}H_{38}$			77.6			22.2	539	0.20	38.8			34.3
Nonadecane	$C_{19}H_{40}$	70.8		108	259		24.9	550	2.26	60.0			
Eicosane	$C_{20}H_{42}$	25.8	42.9	112	160	12.7	29.8	694	66.6	131	165	52.2	
Heneicosane	$C_{21}H_{44}$			122		27.9	31.8	93.9	1.31	160	2.24	0.0	14.7
Docosane	$C_{22}H_{46}$	7.91	20.5	129	22.8	0.56	52.9	116	57.8	148	0	40.0	
Tricosane	$C_{23}H_{48}$	8.73		92.6	5.05	0.67	34.9	104	64.3	124	206		
Tetracosane	$C_{24}H_{50}$		21.1	91.1	113		43.5		26.7	79.1	194		
Pentacosane	$C_{25}H_{52}$			115			41.3	9.71	34.4	98.2	162		
Hexacosane	$C_{26}H_{54}$	182		119	98.4		51.3	65.1	28.2	69.9			
Heptacosane	$C_{27}H_{56}$		1.55	26.8		0.83	23.7		2.72	2.23			7.62
Octacosane	$C_{28}H_{58}$		13.0	213	57.5	4.72	211		34.0	114		4.05	5.42
Nonacosane	$C_{29}H_{60}$	132		525	339	77.0	357	264	347	611	126	16.4	42.9

Hentriacontane	$C_{31}H_{64}$	70.9		1823	253	84.8	326	97.1	82.0	807	43.8	12.5	29.5
Dotriacontane	$C_{32}H_{66}$			117	139	10.7	29.6	31.7	0.36	53.5		11.3	1.09
Tritriacontane	$C_{33}H_{68}$			269	88.7	40.5	210	31.1	16.8	105			
Tetratriacontane	$C_{34}H_{70}$			3.74			6.41		1.00				
Pristane	$C_{19}H_{40}$		0.02		2088	4.39	7.02	2450	48.9	62.0	135	10.7	53.9
Alkene													
Dodecene	$C_{12}H_{24}$		4.58	1.39	4.49	2.22	0.36	29.5	1.27	0.84	19.5	46.0	0.53
Tridecene	$C_{13}H_{26}$	8.42											0.13
Tetradecene	$C_{14}H_{28}$	2.39	8.20	2.03	13.6	9.26	1.77	400	2.75	1.13	41.6	8.25	5.45
Pentadecene	$C_{15}H_{30}$			21.0		3.12	2.65	304	1.70	12.5		3.69	21.7
Hexadecene	$C_{16}H_{32}$	509	7.43	9.42	301	26.8	4.71	795	2.90	0.19	135	53.3	46.9
Heptadecene	$C_{17}H_{30}$	5998	14.8	128	3245	135	16.2	3120	5.46	71.0			1 088
Octadecene	$C_{18}H_{36}$	4332	87.9	133	4869	208	27.3	5047	9.61	94.3	1513	420	48.0
Nonadecene	$C_{19}H_{38}$	728	220	88.1	2757	373	65.3	7373	24.2	8.12	1333	265	
Eicosene	$C_{20}H_{40}$		164	226	88.3	130	116	1773	190	281	124	157	
Heneicosene	$C_{21}H_{42}$		17.5	51.3	184	45.6	45.7		21.0	7.14		57.7	
Docosene	$C_{22}H_{44}$	41.1	16.4	268	158	47.7	76.8	173	30.6	148	61.8	40.5	
cis-9-Tricosene	$C_{23}H_{46}$	299	13.3	269	104	35.5	59.1	63.6	17.1	158	37.0	23.1	
Tetracosene	$C_{24}H_{48}$		13.1	167	82.8	26.8	97.9	30.0	66.0	164		14.6	
Pentacosene	$C_{25}H_{50}$			160	75.6	28.1	93.0	26.3	61.2	125			
Hexacosene	$C_{26}H_{52}$			1097	65.1	28.9	623		71.5	807			
Heptacosene	$C_{27}H_{54}$			140	47.0	22.4	72.9		11.0	63.8			
Octacosene	$C_{28}H_{56}$	12.3	68.7	169	176	32.9	36.8		83.7	154			9.48
Nonacosene	$C_{29}H_{58}$			34.5						24.6			
Triacontene	$C_{30}H_{60}$			28.9			71.5			2.55			
Dotriacontene	$C_{32}H_{64}$						21.2						2.96
Tritriacontene	$C_{33}H_{66}$					2.48	2.64		1.89	0.39			
Tetratriacontene	$C_{34}H_{68}$			29.5						21.0			
Pentatriacontene	$C_{35}H_{68}$				34.7								
Squalene	$C_{30}H_{50}$	884	180	42.7	844	75.4	127	54.0	20.9	30.5	68.6	210	31.9

PAHs													
Naphthalene	$C_{10}H_8$		92.5	259	12.5	3.24	25.3	1306	38.9	8.38		208	11.6
Acenaphthylene	$C_{12}H_8$	6.09	0.03	85.0	86.3	1.42	80.7	11.5	69.6	7.93	1.30	0.34	88.5
Acenaphthene	$C_{12}H_{10}$			10.4	16.6		5.65	7.68	6.57	2.09		0.02	10.8
Fluorene	$C_{13}H_{10}$	43.3		53.9	375	8.99	64.4	22.2	66.9	61.0		9.72	94.3
Phenanthrene	$C_{14}H_{10}$	2 363	3.92	269	8713	299	55.2	1835	433	141	2379	108	614
Anthracene	$C_{14}H_{10}$	531	2.17	64.1	1742	56.7	171	51.5	164	76.1	510	18.4	237
Fluoranthene	$C_{16}H_{10}$	68.0	27.1	75.0	1796	187	295	1435	325	246	1271	184	230
Pyrene	$C_{16}H_{10}$	53.6	16.0	77.2	1620	206	340	1751	384	249	1048	164	257
p-terphenyl	$C_{18}H_{14}$		1.54		8.46	2.31		32.3	6.29		5.34	2.86	3.41
Retene	$C_{18}H_{18}$		4.39		45.6	8.63	17.1				3.43	7.96	
Benzo[a]anthracene	$C_{18}H_{12}$	2.75	3.66	19.5	87.3	28.4	56.6	25.2	65.2	248	24.3	7.88	42.6
Chrysene	$C_{18}H_{12}$	23.9	9.53	48.2	134	39.5	76.5	29.5	78.5	30.7	34.7	10.4	52.4
Benzo[a]fluorantene	$C_{20}H_{12}$			1.77		2.43	1.73		2.51	1.26			
Benzo[b]fluoranthene	$C_{20}H_{12}$	3.45	2.03	7.89	40.1	15.9	30.2	19.6	34.7	22.5	8.33	2.58	18.2
Benzo[k]fluoranthene	$C_{20}H_{12}$	0.87	0.60	3.54	23.1	8.66	18.2	7.92	23.4	16.7	4.13	1.04	8.38
Benzo[j]fluoranthene	$C_{20}H_{12}$				10.8	6.21	3.14	2.63	21.4	14.4		0.20	6.18
Benzo[a]pyrene	$C_{20}H_{12}$		0.62	7.91	29.8	12.6	26.7	10.2	26.6	8.28	3.05	1.17	9.00
Benzo[e]pyrene	$C_{20}H_{12}$									1.10			12.8
Perylene	$C_{20}H_{12}$		0.33	1.23	6.96	2.61	4.30	0.47	4.80	1.28		0.32	2.18
Dibenzo[a,h]anthracene	$C_{22}H_{14}$		0.22	0.58	1.89	1.12	1.73	1.11	1.81	9.11		0.14	0.86
Benzo[ghi]perylene	$C_{22}H_{14}$			1.75	13.1	4.99	6.20	2.27	6.40	1.57	1.14	0.36	3.19
PAHs alkyl derivatives													
Cyclopenta[c,d]pyrene	$C_{18}H_{10}$	117	11.1	12.7		4.73	4.94		16.2	6.86			3.68
Acephenanthrylene	$C_{16}H_{10}$			7.63	100	16.4	9.49	38.1	11.4	5.44	49.8	10.6	7.94
Methylnaphthalenes	$C_{11}H_{10}$			343			91.5	1017	98.4	244			177
Methylfluoranthenes	$C_{17}H_{12}$	132		55.5	1 949	33.1	134		45.7	40.6	490	14.3	110
Methylphenantrenes	$C_{15}H_{12}$			10.1			5.45		12.1	7.18	173		
Dimethylphenantrene	$C_{16}H_{14}$			12.0		4.84	2.64		5.37	10.1		8.03	

Methylchrysenes	$C_{19}H_{14}$						3.42		7.77				
Carbonyls													
Decanal	$C_{10}H_{20}O$		69.7	27.5	17.7	222		77.3				391	
5-Hydroxymethylfurfural	$C_6H_6O_3$	0.10	0.42	0.14	0.22		0.05	0.34				1.77	0.14
2,5-Dihydroxybenzaldehyde	$C_7H_6O_3$		348										
Decan-2-one	$C_{10}H_{20}O$											25.9	0.61
Tridecan-2-one	$C_{13}H_{26}O$	0.11	6.49	4.29	0.31	2.74	2.95	12.7	5.51	0.13		322	5.06
Pentadecan-2-one	$C_{15}H_{30}O$	0.88	121	20.9	0.82	7.02	16.5	702	16.1	2.79	3.93	435	14.5
Hexadecan-2-one	$C_{16}H_{32}O$	48.6	298		107	399		1477	140		42.1	1251	111
Heptacosan-2-one	$C_{17}H_{34}O$			37.9			20.1		21.6	20.3			11.1
Octadecan-2-one	$C_{18}H_{36}O$		11.9	14.0	0.25	4.20	11.4	20.2	19.8	3.61	0.40	40.7	12.2
15-nonacosanone	$C_{29}H_{58}O$				198	225	431	3.53	266	198		9.02	54.6
2-Pentadecanone, 6,10,14-trimethyl-	$C_{18}H_{36}O$	133	256	1119	165	171	254	5465	90.3	83.8		1639	38.8
Other n-alkan-2-ones			361	55.8		180				39.8		680	
Fluoren-9-one	$C_{13}H_8O$	9.85	34.0	101	0.40	45.3	130	595	459	75.5	0.69	520	62.6
Anthraquinone	$C_{14}H_8O_2$		9.20				5.09	134	39.6	7.80	6.55	70.4	6.50
2,6-ditert-butylcyclohexa-2,5-diene-1,4-dione (2,6-di-tert-butyl-1,4-benzoquinone)	$C_{14}H_{20}O_2$		59.4	8.99		112	9.74	31.5		1.95		415	5.10
Diphenylmethanone (Benzophenone)	$C_{13}H_{10}O$		17.4				2.89					49.5	
n-alkanols													
1-Decanol	$C_{10}H_{22}O$								201			67.8	
n-Dodecanol	$C_{12}H_{26}O$		67.5								2738	5309	
n-Tridacanol	$C_{13}H_{28}O$		62.1										
n-Tetradecanol	$C_{14}H_{30}O$		143			95.5						2404	
n-Hexadecanol	$C_{16}H_{34}O$		771			400				130		9087	90.5
n-Octadecanol	$C_{18}H_{38}O$		4501	10092		2140	931		1014	585	130		1744
n-Eicosanol	$C_{20}H_{42}O$			98.9	346	80.8	195			278			203

n-Docosanol (behenyl alcohol)	$C_{22}H_{46}O$		245	3434		847	2365	996	2172	2156		252	1883
n-Tricosanol	$C_{23}H_{48}O$		173	2725	504	488	1346	245	790	770		77.6	831
n-Tetracosanol	$C_{24}H_{50}O$			443	372	2044	211	515	235	182	700		
n-Pentacosanol	$C_{25}H_{52}O$	1690		668	273	89.6	289	179	204	187	66.4	65.0	192
n-Hexacosanol	$C_{26}H_{54}O$	841		1013	2151	789	1659	1143	736	702			508
n-Heptacosanol	$C_{27}H_{56}O$	152	38.3	995	381	132	301	280	307	279	131	7.33	258
n-Octacosanol	$C_{28}H_{58}O$	714	221	4744	2795	1010	2259	2131	2492	2176	1086	121	2166
n-Nonacosanol	$C_{29}H_{60}O$								150				88.7
n-Tricontanol	$C_{30}H_{62}O$	257	50.3	1136	1179	410	741	1154	1534	1220	575	49.5	781
Other Alcohols													
2-Methylcyclohexan-1-ol	$C_7H_{14}O$			2.12									
Propan-1,2,3-triol (Glycerol)	$C_3H_8O_3$	879	44.3	3911	424	230	886	936	2383	7501	1403	218	914
2-[2-(2- Hydroxyethoxy)ethoxy] ethanol Triethylene glycol (Triethylene glycol)	$C_6H_{14}O_4$	530									1068	287	
Terpenoides													
7,7-Dimethylbicyclo[3.1.1] heptan-4-one (Nopinone)	$C_9H_{14}O$						57.4			250			
6,6-Dimethylbicyclo[3.3.1]hept-2- en-2-carboxaldehyde (Myrtenal)	$C_{10}H_{14}O$						558						5.65
(1R)-cis-4,6,6-Trimethylbicyclo-[3.1.1]hept-3-en-2-one (Verbenone)	$C_{10}H_{14}O$						64.6						28.8
1,3,3-Trimethyl- 2-oxabicyclo[2,2,2]octane (Eucalyptol)	$C_{10}H_{18}O$	463	122	577	839	82.9	123	4751	477		4537	307	193
(2E,7R,11R)-3,7,11,15-Tetramethyl-2-hexadecen-1-ol (Phytol)	$C_9H_{14}O_4$			2449		98.1	479	1570	1659	1753	494		922
Pinic acid	$C_9H_{14}O$		2407	88.3									
cis-Pinonic acid	$C_{10}H_{16}O$		42.6	331		41.3	51.7	536	151	114	185	38.7	

n-alkanoic acids													
Hexanoic acid (Caproic acid)	$C_6H_{12}O_2$			137	329				32.8	31.0			8.52
Heptanoic acid	$C_7H_{14}O_2$			260	256	17.4	36.3	1188	51.2	70.1		2033	
Octanoic acid (Caprylic acid)	$C_8H_{16}O_2$		30.5	298	226	186	98.2	5442	64.8	97.6	2058	13.9	55.2
Nonanoic acid (Pelargonic acid)	$C_9H_{18}O_2$		32.0	7.65		132	1.72	2325	41.2	2.51	745	39.2	47.6
Decanoic acid (Capric acid)	$C_{10}H_{20}O_2$	153	71.4	75.5		101	5.32	630	0.26	4.75		116	1.48
Undecanoic acid	$C_{11}H_{22}O_2$		59.6			27.0		67	3.82	3.29	64.8	46.2	0.00
Dodecanoic Acid	$C_{12}H_{24}O_2$	4542	380			132	38.7	2194	18.9	5.01	46.7	79.0	0.00
Tridecanoic acid	$C_{13}H_{26}O_2$		132	21.7		44.5		52.3	21.4	22.2	85.0	44.9	5.86
Tetradecanoic acid (Myristic acid)	$C_{14}H_{28}O_2$	388	560	8105		286	478	599	332	247	859	194	219
Pentadecanoic acid	$C_{15}H_{30}O_2$		265	17.6		153	4.91	293	11.9	3.25		94.8	1.96
Hexadecanoic acid (Palmitic acid)	$C_{16}H_{32}O_2$		2973	14279	2211	2166	4115	10292	672	4445	1628	3411	3249
Heptadecanoic acid	$C_{17}H_{34}O_2$		105	432		98.5	218	206	183	196	0.00	24.0	125
Stearic acid (Octadecanoic acid)	$C_{18}H_{36}O_2$	5832	2803	478	2113	1089	1726	3819	747	700	1725	3254	793
Nonadecanoic acid (Margaric acid)	$C_{19}H_{38}O_2$	4.73	32.3	3.98		52.6	6.06	81.6			16.4	13.6	1.01
Arachidic acid (Eicosanoic acid)	$C_{20}H_{40}O_2$	694		2025	15316	829	2159	574	479	478	234	20.4	530
Docosanoic acid (Behenic acid)	$C_{22}H_{44}O_2$	319	39.3	42.0	114	531	1445	677	877	855	255	8.68	6.72
Tetracosanoic acid (Lignoceric acid)	$C_{24}H_{48}O_2$	273	19.2	57.1	10.7	539	45.3	871	1032	942	332	7.75	750
Unsaturated acids													
(9Z)-Octadec-9-enoic acid *(*Oleic acid)	$C_{18}H_{34}O_2$	12587	499	3665	1804	2127	929	7633	1774	2309	4235	955	2080
cis, cis-9,12-Octadecadienoic acid (Linoleic acid)	$C_{18}H_{32}O_2$	20852	578	66561	1301	1443	5486	7715	6978	6618	978	84.2	3064
trans-9-Hexadecenoic (Palmitelaidic acid)	$C_{16}H_{30}O_2$		36.8	161			67.7	285			373	16.7	66.7
cis-9-Hexadecenoic (Palmitoleic acid)	$C_{16}H_{30}O_2$	335	24.3			26.2							

Dicarboxylic acid													
Propanedioic acid (Malonic acid)	$C_3H_4O_4$		687	12.4			6.60		19.3	9.53			
Butanedioic acid (Succinic acid)	$C_4H_6O_4$		322	71.5		127	438		219	82.4		225	62.1
Pentanedioic acid (Glutaric acid)	$C_5H_8O_4$		134	19.7		71.8	188		112	68.3		41.8	35.5
Hexanedioic acid (Adipic Acid)	$C_6H_{10}O_4$		209	4.13		38.1	15.2	63.7	24.7	35.9		62.8	
Heptanedioic acid (Pimelic acid)	$C_7H_{12}O_4$	1346	143	1 511	305	248	1702	1 126	2 177	1025	552		465
Octanedioic acid (Suberic acid)	$C_8H_{14}O_4$		26.0				99.2	14.2	215			8.15	
Nonanedioic acid (Azelaic acid)	$C_9H_{16}O_4$		55.3	71.6		14.0	126	49.2	69.1	43.7		13.3	30.8
Decanedioic acid (Sebacic acid)	$C_{10}H_{18}O_4$	234	24.4	6.79		3.72	20.6		14.3	8.20			6.04
Hexadecanedioic acid (Thapsic acid)	$C_{16}H_{30}O_4$		4.62	5.42		3.32	10.1	13.4	30.4	23.0		0.91	6.25
Methylmalonic acid	$C_4H_6O_4$	145	28.3	9.97	102	15.9	0.56	125	2.60	0.71	123	5.66	0.22
Hydroxybutanedioic acid (Malic acid)	$C_4H_6O_5$	158	34.7	2.44		10.1	5.88		5.08	2.26	491	6.67	0.87
1,2-Benzenedicarboxylic acid (Phthalic acid)	$C_8H_6O_5$		21.5	25.1		21.7	46.1	24.0	17.1	74.2	5.78	304	1352
Terephthalic acid (1,4-Benzenedicarboxylic acid)	$C_8H_6O_5$	431											
Other phtalates		653	1435		101582	2691	239	18013	504	440	10524	11367	560
Oxo- and hydroxy-acids													
2-Hydroxypropanoic acid (Lactic acid)	$C_3H_6O_3$	243	61.3	755	575		437	2050	4512	1153	1365	3522	163
3-Hydroxypropanoic acid (Hydracrylic acid)	$C_3H_6O_3$					135							
2-Hydroxyethanoic acid (Glycolic acid)	$C_2H_4O_3$	563	987		396		789		245	151	409		195
4-Oxopentanoic acid (Levulinic acid)	$C_5H_8O_3$	371	210	474	185	273	995	204	759	489	258	202	209
Alpha-Hydroxyusobutyric acid	$C_4H_8O_3$									187	127	31	24.7
3-Hydroxy-2-methylpropanoic acid (3-hydroxybutyric acid)	$C_4H_8O_3$		70.4	16.2		44.2	15.0	55.3	23.1	11.3	48.3	43.0	7.19
4-Hydroxybenzoic acid	$C_7H_6O_3$		28.2	86.4		10.9	144	34.2	162	168		63.8	38.0
(E)-3-Phenylprop-2-enoic acid	$C_9H_8O_2$		240	269	67.8	63.2	273	305	442	289	75.2		127

(trans-Cinnamic acid)													
3-(2,3-Dihydroxyphenyl)propanoic acid (Hydrocinnamic acid)	$C_9H_{10}O_4$						235						
2,3-Dihydroxypropanoic acid (Glyceric acid)	$C_3H_6O_4$		148			18.9		44.8				57.8	
Other acids													
Benzoic acid	$C_7H_6O_2$	106	224	548	202	323	729	14073	936	17.3	5910	363	660
Furan-2-carboxylic	$C_5H_4O_3$					21.7	79.2		99.1	322			32.6
(3-Carboxy-3-hydroxypentanedioic acid) Citric acid	$C_6H_8O_7$	1568	288			83.0							
3-(2,3-Dihydroxyphenyl)propanoic acid (Hydrocinnamic acid, 3,4-dihydroxy-)	$C_9H_{10}O_4$								249	179			85.2
Isopimaric acid	$C_{20}H_{30}O_2$	200	56.6			64.2					177	53.6	
Abieta-7,13-dien-18-oic acid (Abietic acid)	$C_{20}H_{30}O_2$		282		1 935			378			46.0	66.5	
Acids ni		3742	904	274		191	174	911	204	190	63.5	162	91.9
Phenolic compounds													
Phenol	C_6H_6O			2560									
Benzene-1,2,3-triol (Pyrogallol)	$C_6H_6O_3$						514		778	3894			156
Benzene-1,2-diol (Catechol)	$C_6H_6O_2$		382	11061	12179	2502	12625	173270	15044	21700	42059	9160	851
Benzene-1,3-diol (Resorcinol)	$C_6H_6O_2$					326	1018		4504	15938			66.3
Benzene-1,4-diol (Hydroquinone)	$C_6H_6O_2$			6150									620
4-hydroxybenzaldehyde	$C_7H_6O_2$					231							
(Methylphenols) Cresols	C_7H_8O		52.7	5.13		21.4	1.56	197	6.10	2.16	982	165	6.64
2-Methoxyphenols	$C_7H_8O_2$			747		31.4	172	3871	344	725	3514	1786	245
Methoxyphenols (Methylcatechols)	$C_7H_8O_2$			5221		512	8051	109743	10861	12424	59625	9012	2500
4-Hydroxy-3-	$C_8H_8O_3$	15970	837	1288	6073	879	2174	31345	1727	2199	43758	20547	1143

methoxybenzaldehyde (Vanillin)													
4-Hydroxy-3-methoxybenzoic acid (Vanillic acid)	$C_8H_8O_4$	161	42.9	58.4		135	371	1714	350	170	2825	251	81.9
2,6-Dimethylphenol	$C_8H_{10}O$				5459				162		2257	2039	128
3,5-Dimethylphenol	$C_8H_{10}O$	1057		1103			478	1758	609	753	28617	11327	522
3-Phenylpropanoic acid (Hydrocinnamic acid)	$C_9H_{10}O_2$						235						
4-Hydroxy-3,5-dimethoxybenzaldehyde (Syringaldehyde)	$C_9H_{10}O_4$	0.28	0.45	42.7	0.16	430	9.50	3979	63.9	66.8	1401	2.71	5.73
Hydroxy(4-hydroxy-3-methoxy-phenyl)acetic acid (Vanillylmandelic acid)	$C_9H_{10}O_5$	1287	188		1387	32.6		837				125	
4-Hydroxy-3,5-dimethoxybenzoic acid (Syringic acid)	$C_9H_{10}O_5$		7.99	74.8		110	693	417	547	301	114	116	87.9
4-Allyl-2-methoxyphenol (Eugenol)	$C_{10}H_{12}O_2$			630			376	2164	520	835	1442		
1-Hydroxy-2-methoxy-4-propenylbenzene (Isoeugenol)	$C_{10}H_{12}O_2$	2170		2975	2407	320	1856	55981	2402	4078	6172	1828	178
3-(4-Hydroxy-3-methoxyphenyl)prop-2-enal (Coniferyl aldehyde)	$C_{10}H_{10}O_3$		12.5		0.74	42.8		43.6				3.01	
4-(3-Hydroxy-1-propenyl)-2-methoxyphenol (Coniferyl alcohol)	$C_{10}H_{12}O_3$			2261		99.5	4438		1998	2374	305	16.2	989
(E)-3-(4-Hydroxy-3-methoxy-phenyl)prop-2-enoic (Ferulic acid)	$C_{10}H_{10}O_4$						31.2		18.5	21.5			
4-Hydroxy-3,5-dimethoxycinnamyl alcohol (Sinapyl alcohol)	$C_{11}H_{14}O_4$			60.8			110			152			18.5
3-(4-Hydroxy-3,5-dimethoxyphenyl)prop-2-enoic acid (Sinapic acid)	$C_{11}H_{12}O_5$	1826	53.8			2.99	16.6			25.9	277	27.6	6.64
Methyl ester acids													

Methyl pentadecanoate (Pentadecanoic acid methyl ester)	$C_{16}H_{32}O_2$				51.1			834			5.75	36.3	
Propan-2-yl tetradecanoate (Tetradecanoic acid 1-methylethyl ester)	$C_{17}H_{24}O_2$	241			276	107		859			1.72	164	
Methyl hexadecanoate (Hexadecanoic acid methyl ester)	$C_{17}H_{32}O_2$		177	412	290	171	114	7498	246	199		751	198
Methyl octadecanoate (Octadecanoic acid methyl ester)	$C_{19}H_{38}O_2$		85.6	150		57.7	45.5		47.1			52.3	
Methyl icosanoate (Eicosanoic acid methyl ester)	$C_{21}H_{42}O_2$			61.2		16.7	38.3		56.2			46.0	28.3
Methyl docosanoate (Docosanoic acid methyl ester)	$C_{22}H_{44}O_2$			75.9		28.0	33.9	87.4	54.5	55.4			52.0
Methyl docosanoate (Tricosanoic acid methyl ester)	$C_{23}H_{46}O_2$			57.1		7.45	24.1	37.8	49.9	39.1			40.8
Methyl tetracosanoate (Tetracosanoic acid methyl ester)	$C_{24}H_{48}O_2$	125		73.4	95.8	24.8	57.9	110	110	97.9			65.3
Methyl pentacosanoate (Pentacosanoic acid methyl ester)	$C_{25}H_{50}O_2$						13.0			19.9			16.0
Methyl pentacosanoate (Hexacosanoic acid methyl ester)	$C_{26}H_{52}O_2$			18.0			26.0		25.8	25.1			8.35
Methyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoate (Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester)	$C_{18}H_{28}O_3$		32.6									8.22	
Alkyl ester acids													
Tetradecanoic acid alkyl ester			148		29.8	64.5							
Hexanoic acid alkyl ester			37.5			13.3						19.1	
Octadecanoic acid alkyl ester			421			34.9							
Octadecyl icosanoate (Eicosanoic acid octadecyl ester)	$C_{38}H_{76}O_2$		781									83.2	
Dioctyl hexanedioate (Hexanedioic acid dioctyl ester)	$C_{22}H_{42}O_4$	5.16	182	174	3296							3081	

Ethyl 4-ethoxybenzoate (Benzoic acid, 4-ethoxy-, ethyl ester)	$C_{11}H_{14}O_3$				5068						10388		
Benzoic acid alkyl ester			15.3									43.6	
Steroid hydrocarbons and derivatives													
(2R)-2,5,7,8-Tetramethyl-2-[(4R,8R)-(4,8,12-trimethyltridecyl)]-6-chromanol (α-Tocopherol/Vitamin E)	$C_{29}H_{50}O_2$			342	46.3	50.5	195	634	3401	1704	52.1	8.32	94.4
Stigmasterol	$C_{29}H_{48}O$	133		729	438	154	505	154	193	140	93.6	6.21	206
b-Sitosterol	$C_{29}H_{50}O$	891	137	4276	1697	575	1723	1583	1921	1321	817	56.8	1618
19-Nor-24-methylcholest-5,7,9,22-tetraen-3á-ol (Neoergosterol)	$C_{27}H_{40}O$			1014		223	314		253	199			398
Ergosta-5,7,22-trien-3β-ol (Ergosterol)	$C_{28}H_{44}O$												369
20(29)-Lupen-3-beta-ol (Lupeol)	$C_{30}H_{50}O$								10.6				
α-Tocopherol-β-D-Mannoside	$C_{35}H6_0O_7$			336		12.7	118		284	234			89.6
[(2R)-2,5,7,8-Tetramethyl-2-[(4R,8R)-4,8,12-trimethyltridecyl]chroman-6-yl] acetate ((±)-α-Tocopherol /Vitamin E acetate)	$C_{31}H_{52}O_3$		65.2			7.82	6.46						
5α-Cholestane	$C_{27}H_{48}$								7.82				
3,a,5-Cyclo-5a-ergosta-6,8(14)22-triene	$C_{28}H_{42}$						0.04						
5-α-ergostane	$C_{28}H_{50}$								4.45				
Stigmastan-4,5,22-diene	$C_{29}H_{48}$			10.8									
stigmastan-3,5,22-triene	$C_{29}H_{46}$						65.0	34.5	10.4	2.21			14.5
Stigmastan-3,5-diene	$C_{29}H_{48}$			124			117		117	22.7			
Other steradiens		94.9	20.4	42.2	399	95.4	235	455	95.4	36.9	56.3		
Other steratriens				57.4	32.6	28.1	22.3	114	51.7	12.0			33.3
Other steratetraenes			34.4		5.86	20.7		15.3	5.17				

Hopanoids													
A'-Neogammacer-22(29)-en-3-one (22(29)-hopene)	$C_{30}H_{48}O$						2.26						
Other hopanoids			1120	40.8		31.3	1.15	31.2	40.7	8.02	79.9	84.5	
Sugars/polyols and thear derivatives													
6,8-dioxabicyclo[3.2.1]octane-2,3,4-triol (Levoglucosan)	$C_6H_{10}O_5$	207		3304	109	24572	7844	235	5371	5292		3.27	1973
6,8-dioxabicyclo[3.2.1]octane-2,3,4-triol (Mannosan)	$C_6H_{10}O_5$			3.26			45.4		739	114			31.8
(2R,3R,4S)-Pentane-1,2,3,4,5-pentol (Xylitol)	$C_5H_{12}O_5$			370					124				
β-D-fructofuranosyl-(2→1)-α-D-glucopyranoside (Sucrose)	$C_{12}H_{22}O_{11}$	320	15.4								141	15.9	
butane-1,2,3,4-tetrol (meso-Erythritol)	$C_4H_{10}O_4$			8539					1212				
cis-1,2,3,5-trans-4,6-Cyclohexanehexol (Myo-inositol)	$C_6H_{12}O_6$	22502	233				237						
cis-1,2,4-trans-3,5,6-Cyclohexanehexol (Chiro-inositol)	$C_6H_{12}O_6$	1149											
3-deoxy-D-arabino-hexono-1,4-lactone	$C_6H_{10}O_5$					327			686	710			353
β-D-glucopyranuronic acid (Glucuronic acid)	$C_6H_{10}O_7$	1826	53.8				11.8				26.8		5.55
(2R)-2-[(2S,3R,4S)-3,4-Dihydroxy-5-oxo -tetrahydrofuran-2-yl]-2-hydroxy-acetaldehyde (Glucuronic acid lactone)	$C_6H_8O_6$			6.24				9.23					
ɣ-Heptalactone	$C_7H_{12}O_2$					478			747			470	
Sugars ni		128		241	1555	109	640		813	811		11.0	755

Monoglicerides													
2,3-Dihydroxypropyl tetradecanoate	$C_{17}H_{34}O_4$	513			243						270	23.5	
2,3-Dihydroxypropyl hexadecanoate	$C_{19}H_{38}O_4$			89.5						32.0	1685		19.0
2,3-Dihydroxypropyl octadecanoate	$C_{21}H_{42}O_4$		190	48.9									
2,3-Dihydroxypropyl eicosanoate	$C_{23}H_{46}O_4$	104	137		150	66.7		1308			47.5	55.4	
Other compounds													
Indole + Indole derivative	C_8H_7N								92.5				
s-diphenylethane	$C_{14}H_{14}$							432			852	85.1	15.8
Other Alkyl biphenyls		17.7	47.4	0.06		34.4	21.3		9.31	0.32	191	52.6	56.2

Supplementary Material A4

Table A4 Survey questionnaire.

Question 1. How much wood do you buy/consume per year for heating or cooking purposes?			
a) in euros;			
b) in metric tons;			
c) cubic meters;			
d) do not know/do not answer			
Question 2. What type of wood do you use?			
	What type of wood do you buy/consume?	Amount in ton/m^3	Amount in euro
Portuguese oak			
Maritime pine			
Eucalypt			
Holm oak			
Cork oak			
Willow			
Olive			
Golden wattle			
Ash tree			
Hornbeam			
Beech			
Poplars			
Cherry			
Briquettes/Pellets			
Other, What?			
Question 3. What kind of burning equipment do you use?			
a) Woodstove			
b) Fireplace			
c) Wood burning furnace			
d) “Salamandra”			
e) Ovens			
f) Other, What?			
Question 3.1 If yes, how often?			
a) 1 month			
b) Between 2 and 4 months			
c) Between 5 and 12 months			
d) Throughout the year			
Question 3.2 How many days per week?			
a) 1 day/week			
b) Between 2 and 3 days /week			
c) Between 5 and 7 days /week			

Question 3.3 At what time of the day?			
a) During the morning			
b) During the afternoon			
c) During the lunch			
d) During the dinner			
e) During the evening			
Question 4. How much wood do you burn annually for:			
a) Heating			
b) Cooking			

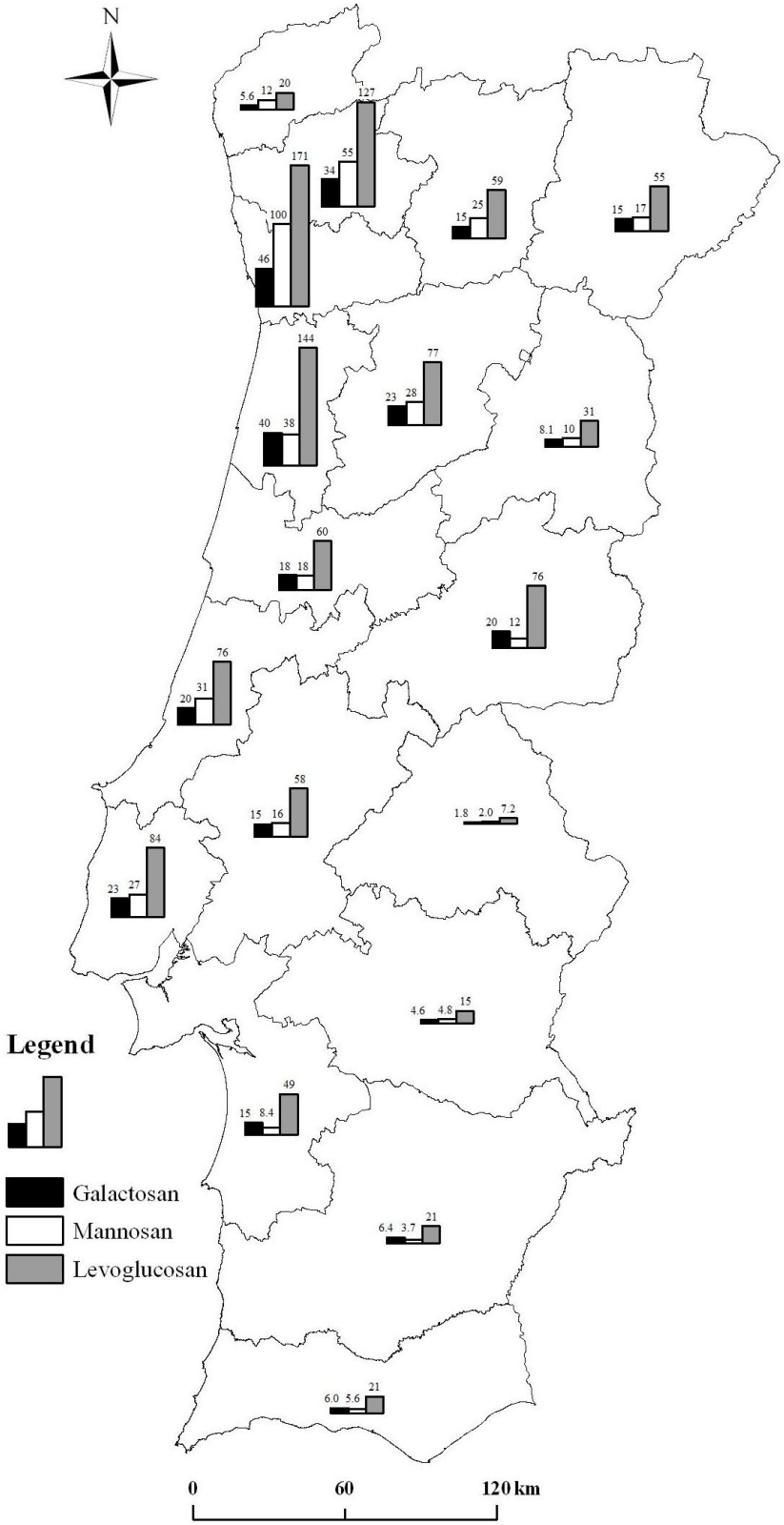

Figure 1S Annual emissions of anhydrosugars (t y^{-1}).

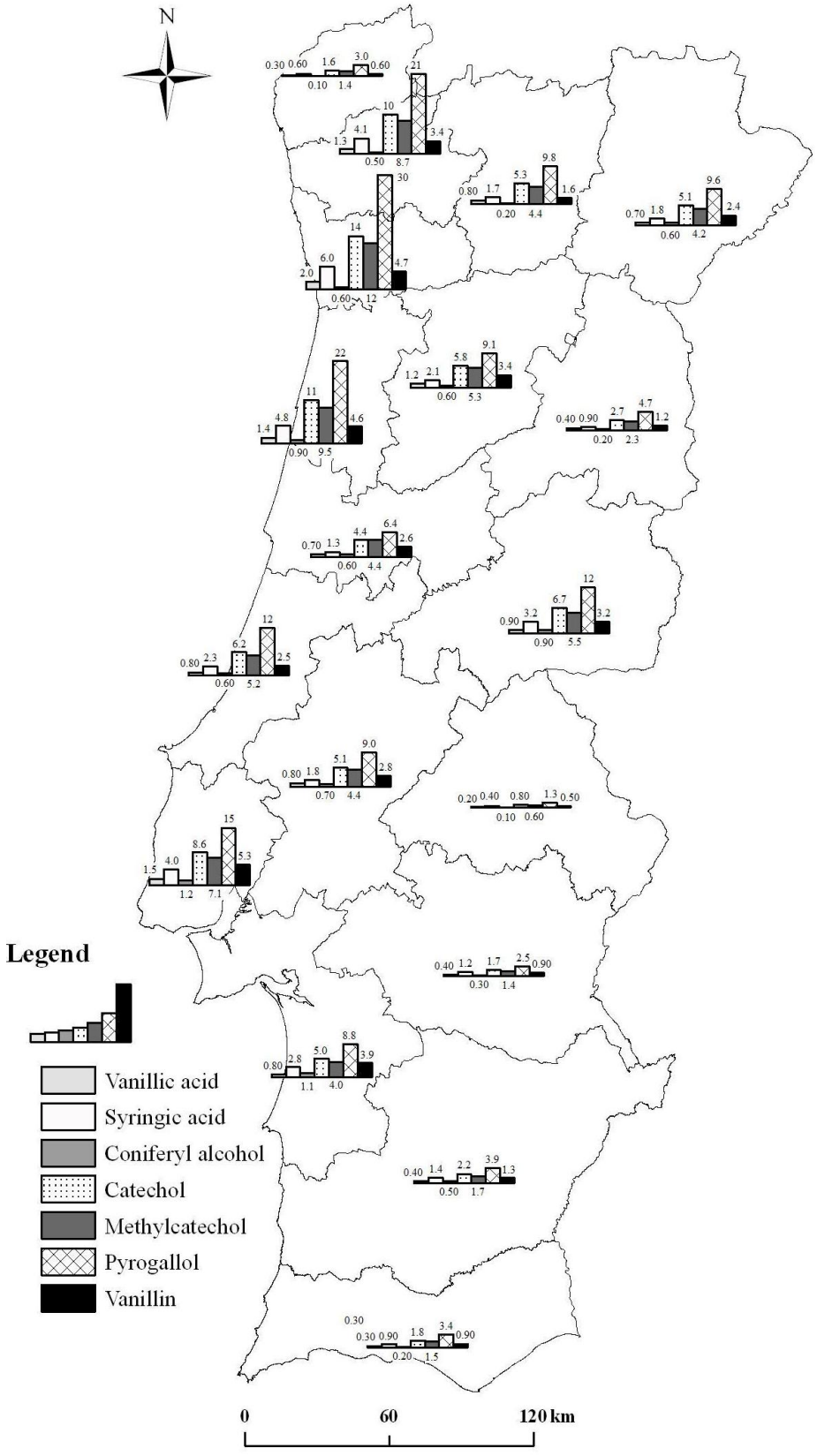

Figure 2S Annual emissions of phenolic compounds (t y^{-1})

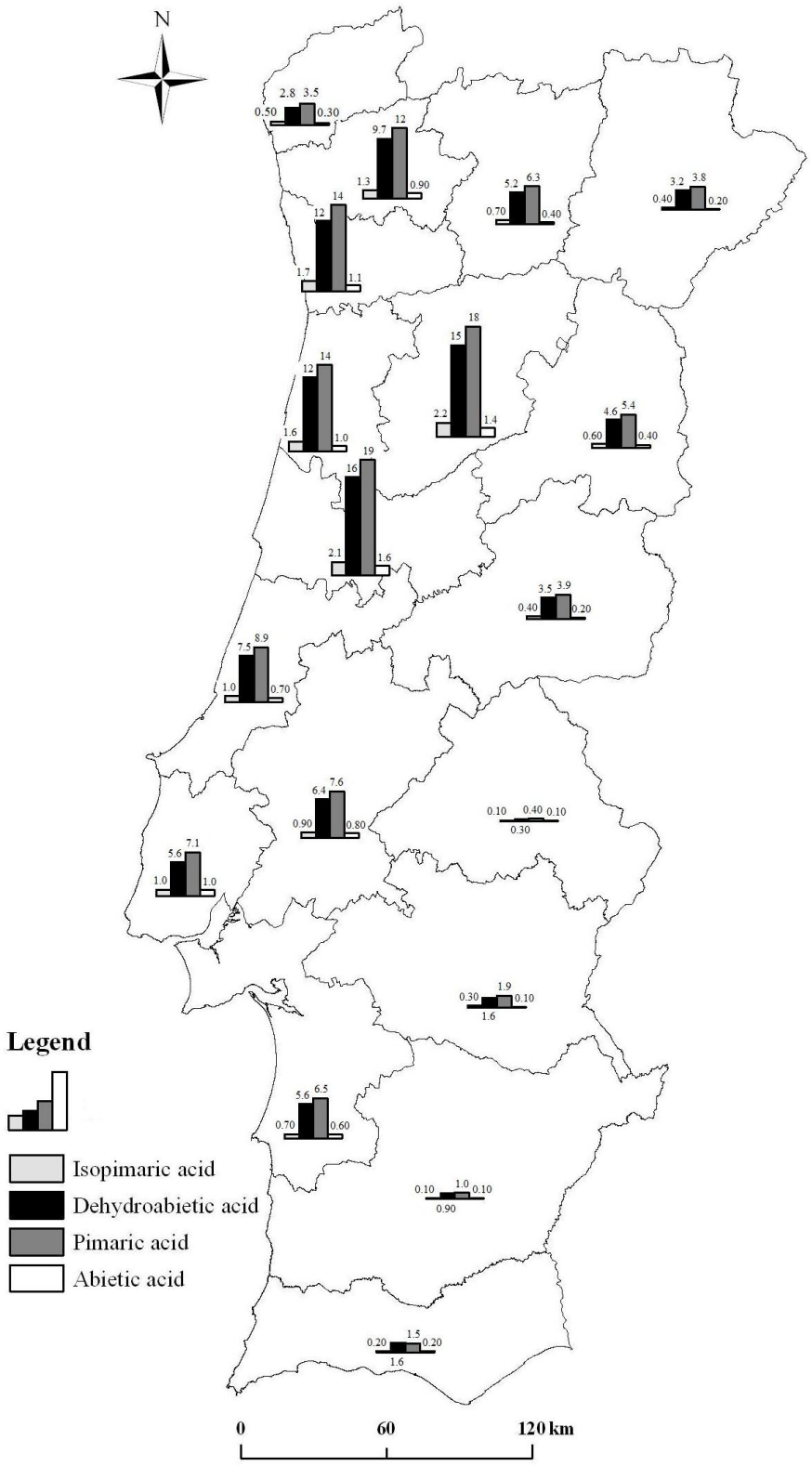

Figure 3S Annual emissions of resin acids by district (t y^{-1}).

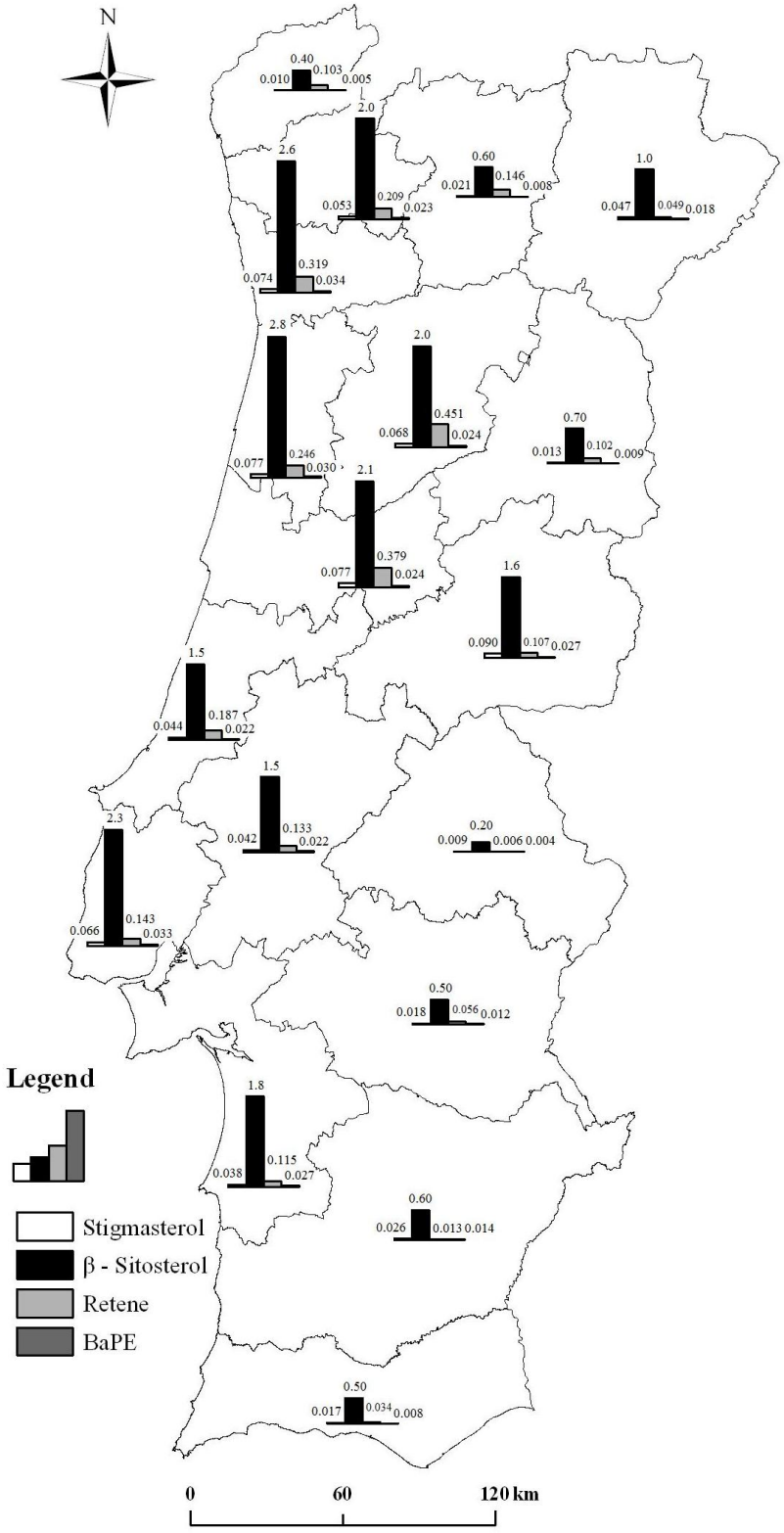

Figure 4S Annual phytosterol and PAH emissions by district (t y^{-1}).